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Organic Chemistry.

Refractive Indices of Hexanes and Hexenes. H. VAN RISSEGHEM (*Bull. Soc. chim. Belg.*, 1924, **33**, 115—119; cf. A., 1922, i, 313).—The following corrected values are given. ββ-Dimethylbutane, n_D^{15} 1·3716, $n_{H\beta}^{15}$ 1·3762, $n_{H\gamma}^{15}$ 1·3801; *iso*hexane, $n_{H\alpha}^{15}$ 1·3725, $n_{H\beta}^{15}$ 1·3792, $n_{H\gamma}^{15}$ 1·3829; γ-methylpentane, n_D^{15} 1·3793, $n_{H\beta}^{15}$ 1·3841, $n_{H\gamma}^{15}$ 1·3878; βγ-dimethylbutane, $n_{H\beta}^{15}$ 1·3855, $n_{H\gamma}^{15}$ 1·38935. H. J. E.

Photochlorination of Aliphatic Compounds in Carbon Tetrachloride. A. BENRATH and E. HERTEL (*Z. wiss. Phot.*, 1924, **23**, 30—40).—The amount of chlorine dissolved in technical or in pure carbon tetrachloride (Kahlbaum) continuously diminishes when the solution is subjected to the action of light. If, however, the carbon tetrachloride has been previously subjected at its boiling point to the prolonged action of chlorine and then purified by treatment with nitric acid followed by sodium carbonate and chlorine again dissolved in it, the chlorine titre no longer diminishes but increases when the solution is subjected to light. Perfectly purified and dried carbon tetrachloride was shown to contain free chlorine after several days' exposure to light. The amount of decomposition is not sufficiently great to hinder the use of carbon tetrachloride as a medium in which to study the photochlorination of various aliphatic compounds. The chlorine solutions employed contained about 0·05 g. of chlorine in 10 g. of solution. In some of the compounds investigated, one atom of hydrogen was displaced, in others two. The reaction was generally preceded by an induction period. The amount of chlorination, in some cases, was proportional to the time and in others to the logarithm of the time. If two atoms of hydrogen are displaced, the reaction takes place in distinct steps. The second displacement frequently takes place with a rapidity much greater than that at the end of the first, and is preceded by a new induction period. Chloroform, after an induction period of about 30 mins., absorbs about 70% of the chlorine required for its conversion into carbon tetrachloride. The reaction is not reversible. Tetrachloroethane was not attacked by chlorine in 3 hours. Acetic acid was converted into monochloroacetic acid with very little tendency for the reaction to proceed further. Acetyl chloride and *iso*butyric acid behave similarly to acetic acid. With propionic acid and ethyl malonate the reaction commenced slowly and then continued at a rate proportional to the time until one atom of hydrogen was displaced. The second atom reacted at a much slower rate and in accordance with the logarithmic law. Two atoms of hydrogen were displaced in the case of *n*-butyric acid, both at the logarithmic rate, the two steps of the reaction being markedly

distinct. The chlorination of ethyl ether proceeded linearly during the displacement of one atom, then, after a slowing up, a second atom was displaced at the logarithmic rate. The induction period was long in the case of acetic anhydride and the reaction was in two phases, but the rate was neither linear nor according to the logarithmic law. A. C.

***tert.*-Butyl Alcohol.** R. R. READ and F. PRISLEY (*J. Amer. Chem. Soc.*, 1924, **46**, 1512—1515).—The vapour of *iso*butyl alcohol is passed over pumice coated with aluminium oxide, contained in an iron tube, at 500—520°, and the *iso*butylene formed is freed from water and unchanged alcohol, and hydrated to *tert.*-butyl alcohol by absorption in 50% sulphuric acid, either directly or from its solution in kerosene. The yield is improved by using a glass catalyst tube at 450—475°. The use of phosphoric acid on coke as the dehydrating catalyst (cf. King, T., 1919, **115**, 1404), even at 210—230°, led to the loss of half the total hydrocarbon by polymerisation. F. G. W.

Preparation of Dialkylethinenyl Carbinols. R. LOCQUIN and S. WOUSENG (*Bull. Soc. chim.*, 1924, [iv], **35**, 597—604; cf. A., 1922, i, 617).—The sodium derivatives of ketones may be obtained with a minimum of condensation by-reactions by adding finely-powdered sodamide gradually to a mixture of the ketone (1 part) and dry ether (4—5 parts) kept thoroughly agitated and cooled for several hours, the ammonia being removed under reduced pressure. γ-Ethyl-Δ^{α}-pentinene-γ-ol, $OH{\cdot}CEt_2{\cdot}C{\equiv}CH$, obtained from sodium diethyl ketone and acetylene by the method previously described, forms an *allophanate*, $Et_2C(C{\equiv}CH)O{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$, fine needles, m. p. 130—131°. *γζ-Diethyl-Δ^{δ}-octinene-γζ-diol*, $OH{\cdot}CEt_2{\cdot}C{\equiv}C{\cdot}CEt_2{\cdot}OH$, m. p. 76°, b. p. 132—135°/14 mm., is formed in small quantity along with the ethinenylcarbinol. On distillation with a little solid potassium hydroxide, it is decomposed quantitatively into acetylene and diethyl ketone. α-*cyclo*Hexyl-Δ^{α}-propinene-γ-ol has m. p. 22°, b. p. 73—75°/15 mm.; *allophanate*, m. p. 197°. *ζ-Methyl-γ-isobutyl-Δ^{ζ}-heptinene-γδ-diol*, $C_4H_9{\cdot}CH(OH){\cdot}C(OH)(C_4H_9){\cdot}C{\equiv}CH$, has m. p. 101—102°. *α-Phenyl-γ-propyl-Δ^{α}-hexinene-γ-ol*, $PhC{\equiv}C{\cdot}CPr_2{\cdot}OH$, b. p. 153—158°/10 mm., is obtained by the action of phenylacetylene on the sodium derivative of dipropyl ketone. F. G. W.

Methylpropylethinenylcarbinol [γ-Methyl-Δ^{α}-hexinene-γ-ol] and its Derivatives. R. LOCQUIN and S. WOUSENG (*Bull. Soc. chim.*, 1924, [iv], **35**, 604—606).—*γ-Methyl-Δ^{α}-hexinene-γ-ol*, $OH{\cdot}CMePr{\cdot}C{\equiv}CH$, obtained by the action of acetylene on sodium methyl *n*-propyl ketone, has b. p. 137°; *allophanate*, m. p. 133°. *δη-Dimethyl-Δ^{ϵ}-decinene-δη-diol*, $OH{\cdot}CMePr{\cdot}C{\equiv}C{\cdot}CMePr{\cdot}OH$, m. p. 60°, b. p. 130—135°/10 mm., is formed in small quantity along with the carbinol. The latter substance combines with water in presence of acid mercuric sulphate with formation of *γ-methylhexan-γ-ol-β-one*, b. p. 166—168° (*semicarbazone*, m. p. 163—164°). F. G. W.

Action of Acetylene on Sodium Compounds of Ketones. Isomeric Transformation of Dialkylvinylcarbinols into ββ-Dialkylallyl Alcohols. S. WOUSENG (*Ann. Chim.*, 1924, [x], **1**, 343—416).—The sodium compound of a ketone, obtained by using sodamide, reacts in ethereal suspension with acetylene under a water-pressure of 500—600 cm. to yield an acetylenic alcohol (cf. Locquin and Wouseng, A., 1922, i, 617, 710; 1923, i, 302). Pinacolin thus affords *methyl*-tert.-*butylethinenylcarbinol* [*γδδ-trimethyl-pentinene-γ-ol*], CMe_3·CMe(OH)·C:CH, an oil with a mint-like odour, b. p. 144°, d_4^{11} 0·8806, n_D^{11} 1·4441; this forms a crystalline *hydrate* of low m. p., an *allophanate* (cf. Behal, A., 1919, ii, 301), needles, m. p. 156° (after drying at 110°), and an *acetate*, b. p. 156—159°. Two, or three, by-products, all presumably stereoisomeric forms of the *glycol*, CMe_3·CMe(OH)·C:C·CMe(OH)·CMe_3 (cf. Dupont, A., 1914, i, 134), are also formed, the viscous oily mixture of b. p. 148—150°/14 mm. being separable into scales, m. p. 88—89°, rhomboidal tablets, m. p. 78°, and another substance (?), m. p. 67—68°. The saturated alcohol, *methylethyl*-tert.-*butylcarbinol*, obtained from the acetylenic compound by treatment with hydrogen in presence of platinum black, or directly from pinacolin and magnesium ethyl iodide, has b. p. 152°, and yields an *allophanate*, m. p. 134—135°. Partial hydrogenation of the acetylenic compound to the ethylenic alcohol, *methyl*-tert.-*butylvinylcarbinol*,

$$CMe_3\cdot CMe(OH)\cdot CH:CH_2,$$

b. p. 144—146°, d_4^{11} 0·8576, n_D^{11} 1·4452, which also possesses a strong mint-like odour, was best effected by the action of hydrogen in presence of reduced nickel (in methyl-alcoholic solution). This substance also forms a *hydrate* of low m. p. and gives an *allophanate*, needles, m. p. 167—168° (decomp.). When treated with acetic anhydride at 140°, or boiling glacial acetic acid, it undergoes a molecular transformation analogous to that of linalool into geraniol and nerol (Forster and Cardwell, T., 1913, **103**, 1338 etc.), thus demonstrating (cf. also the results described below) that this change is a general one for tertiary vinylcarbinols. The primary alcohol so obtained, *γδδ-trimethyl-Δ$^{\beta}$-pentenol*, separated as the hydrogen phthalate (cf. Stephan, A., 1899, i, 68), has b. p. 84°/12 mm., and yields an *allophanate*, m. p. 180—181°. When it is oxidised by a chromic–sulphuric acid mixture, or by atmospheric oxygen and metallic silver, it is converted into *βγγ-trimethyl-Δ$^{\alpha}$-pentenaldehyde*, b. p. 75—78°/15 mm., the *semicarbazone* of which has m. p. 204—205°. This aldehyde is also obtained by direct oxidation of the above ethylenic alcohol, γδδ-trimethyl-Δ$^{\beta}$-pentenol, by chromic–sulphuric acid, in a manner exactly analogous to the formation of geraniol and citral from linalool. Further oxidation affords the *acid*, CMe_3·CMe:CH·CO_2H, m. p. 85—86°, which when treated with warm 80% sulphuric acid is converted into the *lactone* of *γγ-dimethyl-β-hydroxymethylvaleric acid* (cf. Petshnikoff, A., 1902, i, 338), which is also obtained when *ethyl γγ-dimethylvalerate*, b. p. 96—99°/10 mm., prepared from pinacolin and ethyl bromoacetate, is heated with formic acid, no dehydration to the corresponding derivative of acrylic acid taking place in this case.

Dipropyl ketone, treated with sodamide and acetylene, yields *γ-propyl-Δ$^{\alpha}$-hexinen-γ-ol*, $CPr^{a}_{2}(OH)\cdot C{:}CH$, b. p. 69—71°/12 mm., d_4^{11} 0·8691, n_D^{11} 1·4443, the *acetyl* derivative of which has b. p. 82—83°/10 mm., and the *allophanate*, m. p. 143°. As a by-product, the glycol, $CPr_2\cdot C(OH)\cdot C{:}C\cdot C(OH)\cdot CPr_2$ (Dupont, *loc. cit.*), is formed. By reduction as described above, ethyldipropylcarbinol (Tschebotarev and Saytzev, A., 1886, 437) is formed, whilst partial reduction affords *dipropylvinylcarbinol*, b. p. 75—76°/12 mm., the *allophanate* of which has m. p. 102—103°. When this ethylenic tertiary alcohol is boiled with acetic acid and the product saponified, the primary isomeride is obtained, exactly as described above; purified through its hydrogen phthalate, *γγ-dipropylallyl alcohol* has b. p. 99—101°/12 mm., and gives an *allophanate*, m. p. 147—148°. When reduced with hydrogen and platinum black, it yields *γ-propylhexyl alcohol*, b. p. 107—108°, which yields an *allophanate*, needles, m. p. 133—134°, and a *pyruvic* ester, b. p. 140—145°/20 mm., the *semicarbazone* of which has m. p. 116—117°. This saturated alcohol is identical in all respects with that obtained by condensing butyrone with ethyl bromoacetate (by the Grignard reaction), dehydrating the product, *ethyl β-hydroxy-β-propylhexoate*, b. p. 160—165°/85 mm., by heating with formic acid and reducing the resulting *ethyl β-propyl-Δ$^{\alpha}$-hexenoate*, b. p. 122—128°/30 mm., with sodium and alcohol. *β-Propyl-Δ$^{\alpha}$-hexenaldehyde* is obtained by regulated oxidation either of γ-propylhexenol, or of the parent dipropylvinylcarbinol; it has b. p. 75—76°/12 mm., and gives a semicarbazone, m. p. 171—173°.

ζ-Methyl-β-heptanone (Bouveault and Locquin, A., 1905, i, 18) yields *γη*-dimethyloctinene-γ-ol, $CHMe_2\cdot[CH_2]_3\cdot CMe(OH)\cdot C{:}CH$, which has b. p. 187—188°, or 83—85°/10 mm.; this gives an *allophanate*, needles, m. p. 114—115°. Stereoisomeric *glycols* are produced as by-products and are isolated first as an oil of b. p. 183—184°/12 mm., from which crystals of m. p. 66—68° may be separated, and the second component forms the main proportion of a pasty mass melting at about 35°. βζ-Dimethyloctan-ζ-ol, identical with Barbier and Locquin's preparation (A., 1914, i, 833), is obtained by reduction of the acetylenic derivative, whilst regulated reduction produces *methylisohexylvinylcarbinol*, b. p. 89—91°/15 mm., which, like its analogues, is readily converted by treatment with hot acetic acid, and subsequent purification through the hydrogen phthalate, into *γη-dimethyl-Δ$^{\beta}$-octen-α-ol*, $CHMe_2\cdot[CH_2]_3\cdot CMe{:}CH\cdot CH_2\cdot OH$, b. p. 110°/12 mm. When this is reduced, a tetrahydrogeraniol is formed, the allophanate of which has m. p. 117°, the pyruvate, b. p. 140—145°/12 mm., and the semicarbazone of the latter, m. p. 118°. This tetrahydrogeraniol was identical with the product obtained via ethyl β-hydroxy-βζ-dimethyloctoate (cf. Bouveault and Blanc, A., 1905, i, 11). *Dihydrocitral*,

$$CHMe_2\cdot[CH_2]_3\cdot CMe{:}CH\cdot CHO,$$

obtained by oxidising either the vinylcarbinol or its primary isomeride, yields a *semicarbazone*, m. p. 164°. The above results show that no conclusion can be drawn from the results of a chromic-sulphuric acid oxidation as to the presence of a primary alcoholic

grouping; catalytic oxidation, on the other hand, gives trustworthy results. The author discusses the mechanism of these isomeric transformations and describes experiments which indicate that Tiemann's explanation (A., 1894, i, 83) is unsatisfactory. W. A. S.

Constitution of Farnesol. Synthesis of Dihydrofarnesol, a new Aliphatic Sesquiterpene Alcohol. A. VERLEY (*Bull. Soc. chim.*, 1924, [iv], **35**, 606—608).—Farnesal, obtained by the oxidation of farnesol with chromic acid, yields, on boiling with 10% potassium carbonate solution, acetaldehyde and dihydro-ψ-ionone, and on reducing the glycidic ester of this compound or that of ψ-ionone with sodium and amyl alcohol, *dihydrofarnesol*,

$CH_2{:}CMe{\cdot}[CH_2]_3{\cdot}CMe{:}CH{\cdot}[CH_2]_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}OH$,

is obtained as an oily, amber liquid with an odour of cedar wood. F. G. W.

Stereoisomerism among Trisubstituted αβ-Glycols and the Production of Stereoisomerides by inverting the Order of Introduction of the Substituent Radicals. M. TIFFENEAU and J. LEVY (*Compt. rend.*, 1924, **178**, 1724—1726).—The products obtained by treating ketols of the general formula CHPh(OH)·CO·R with magnesium alkyl bromides, MgR′Br, are different from those formed when MgRBr acts on CHPh(OH)·CO·R′. The former (R being smaller than R′) are provisionally termed α, the latter β. The α-*variety* of αβ-*dihydroxy*-α-*phenyl*-β-*methylbutane* has m. p. 85°; the β-*variety*, m. p. 73°. Similarly, the α- and β-*forms* of αβ-*dihydroxy*-α-*phenyl*-β-*ethylhexane* have m. p. 88° and 81°, and the α- and β-*ethylhydrobenzoins* have m. p. 105° and 117° respectively. The isomeric forms of these substances yield the same product when dehydrated with concentrated sulphuric acid. W. A. S.

Replacement of Acid Radicals in Glycerides. K. H. BAUER (*Ber.*, 1924, **57**, [*B*], 897—899).—The action of *m*-nitrobenzoyl chloride on glyceryl α-benzoate dissolved in cold chloroform and quinoline (cf. Fischer, A., 1920, i, 808) leads to the production of *glyceryl tri*-m-*nitrobenzoate*, m. p. 160—161° after softening at 158°, in yield which varies with the experimental conditions. H. W.

Preparation of Ethers from Secondary Alcohols by Dehydration with a Sulphonic Acid. R. VERNIMMEN (*Bull. Soc. chim. Belg.*, 1924, **33**, 96—101).—The preparation is easily effected in presence of *p*-toluenesulphonic acid; a high temperature and too great an excess of catalyst should be avoided in order to obviate the formation of ethylenic hydrocarbons. In the aliphatic series, dehydration is more difficult, as the alcohols must be heated nearly to boiling point. The following are described: Di-β-*n*-hexyl ether (cf. Wanklyn and Erlenmeyer, T., 1863, 221), b. p. 200°/760 mm., d_{20}^{20} 0·7889, n_D^{20} 1·4152; *di*-β-n-*amyl ether*, b. p. 160—163°/760 mm., d_{20}^{20} 0·7830, n_D^{20} 1·4078; di(α-phenyl-α-propyl) ether, b. p. 164°/14 mm., d_{20}^{20} 1·0043, n_D^{20} 1·5420 (cf. Oddo and Rosso, A., 1911, i, 443); di(α-phenyl-α-*n*-butyl) ether, b. p. 178—179°/13 mm.,

d_{20}^{20} 0·9769, n_D^{20} 1·5275 (cf. Oddo, *loc. cit.*); di(α-*phenyl*-α-n-*amyl*) *ether*, b. p. 199°/14 mm., d_{20}^{20} 0·9574, n_D^{20} 1·5175. H. J. E.

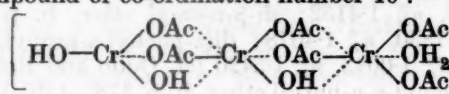
Derivatives of γ-Chloro-*n*-propyl Alkyl Ethers. W. Dulière (*Bull. Soc. chim.*, 1924, [iv], **35**, 584—590).—αγ-Dichloropropyl alkyl ethers (this vol., i, 258) react vigorously with magnesium organohalides with formation of α-substituted γ-chloropropyl alkyl ethers. Of the following compounds described, which are all colourless, strong-smelling oils, the aromatic derivatives are viscous and distil badly under reduced pressure. They are all stable to dilute sodium hydroxide and only slowly attacked by silver nitrate, the mobility of the chlorine atom increasing with increasing molecular weight. γ-*Chloro*-α-*phenyl*-n-*propyl methyl ether*, Me·O·CHPh·CH_2·CH_2Cl, b. p. 110°/12 mm., d^{20} 1·097, n_D^{20} 1·52219; γ-*chloro*-α-*phenyl*-n-*propyl ethyl ether*, b. p. 120°/11 mm., d^{20} 1·066, n_D^{20} 1·51502; γ-*chloro*-α-*phenyl*-n-*propyl* n-*propyl ether*, b. p. 130°/12 mm., d^{20} 1·044, n_D^{20} 1·50492; γ-*chloro*-α-*phenyl*-n-*propyl* iso*butyl ether*, b. p. 137°/11 mm., d^{20} 1·024, n_D^{20} 1·50118; γ-*chloro*-α-*phenyl*-n-*propyl* iso*amyl ether*, b. p. 145°/13 mm., d^{20} 1·019, n_D^{20} 1·50212; *methyl* γ-*chloro*-α-*methyl*-n-*propyl ether*, b. p. 35°/10 mm.; *methyl* γ-*chloro*-α-*ethyl*-n-*propyl ether*, b. p. 40°/10 mm., 147°/atmospheric pressure, d^{22} 0·964, n_D^{22} 1·42501; *ethyl* γ-*chloro*-α-*methyl*-n-*propyl ether*, b. p. similar, d^{22} 0·971, n_D^{22} 1·42751; *methyl* γ-*chloro*-α-iso*propyl*-n-*propyl ether*, b. p. 47°/11 mm., d^{20} 0·951, n_D^{20} 1·43096. α-*Benzyl*-n-*propyl methyl ether*, fine white needles, odour of aniseed, m. p. 34°, b. p. 130°/12 mm., d^{74} 0·983, n_D^{74} 1·54998, was obtained by the action of magnesium benzyl bromide on methyl αγ-dichloro-*n*-propyl ether, instead of the expected γ-chloro derivative. F. G. W.

Alkyl Ethers of Ethylene Glycol. L. H. Cretcher and W. H. Pittenger (*J. Amer. Chem. Soc.*, 1924, **46**, 1503—1504).—Ethylene oxide or ethylene chlorohydrin (1·1 mols.) is added to a solution of sodium (1 mol.) in the appropriate alcohol, the glycol monoalkyl ether being separated by fractionation after removal of the sodium chloride. *Monoisopropyl*, b. p. 144°/743 mm.; *monopropyl*, b. p. 150°/743 mm.; *monoisobutyl*, b. p. 158·8°/743 mm.; *monobutyl*, b. p. 170·6°/743 mm., and *monoamyl glycol ether*, b. p. 181°/745 mm., are described. F. G. W.

Manganese Acetate. A. F. G. Cadenhead and W. H. Vining (*Can. Chem. Met.*, 1924, **8**, 64—65).—Manganese acetate, $Mn(OAc)_2,4H_2O$, rose-pink plates or flat, monoclinic prisms, dissolves to the extent of 64·5 g. in 100 g. of water at 5°.

Chemical Abstracts.

Space Significance of the Co-ordination Number in Polynuclear Compounds. II. Constitution of the Violet Chromic Acetate. H. Reihlen (*Z. anorg. Chem.*, 1924, **133**, 82—90; cf. A., 1921, ii, 193).—The violet chromic acetate is considered to be a compound of co-ordination number 10 :—



S. K. T.

Electrolysis of Mixtures of Acetates and Trichloroacetates. R. E. GIBSON (*Proc. Roy. Soc. Edin.*, 1924, **44**, 140—152).—In the electrolysis of an aqueous solution of potassium acetate and trichloroacetate containing 2 mols. of the former salt to 1 mol. of the latter, the main products are those from single molecules of either acid, namely, ethylene, formaldehyde, and hydrochloric acid. Smaller amounts of derivatives from 2 mols. of either acid, namely, ethane, trichloromethyl trichloroacetate, and hexachloroethane, and from 1 mol. of each acid, trichloromethyl acetate, were also obtained. All reactions resulted in the liberation of carbon dioxide, whilst the formation of carbon monoxide was also observed. A. COUSEN.

Action of Acetic Anhydride on Hydrated Metallic Salts. "Acetylated" Salts. A. RECOURA (*Compt. rend.*, 1924, **178**, 2217—2221).—The action of acetic anhydride on certain hydrated metallic salts is primarily one of dehydration which, in some cases, is complete, but in others certain molecules of water remain combined with the salt and by means of their residual valencies attack molecules of the anhydride. The anhydrous salts do not combine with acetic anhydride. The acetylated salts are generally only stable in an atmosphere of acetic anhydride, and in air rapidly lose their acetic anhydride and unite with water to form the original hydrated salt. The acetylated salt which has lost some acetic anhydride by short exposure to air slowly recombines with it to form the normal acetylated salt when replaced in an atmosphere of the acetic anhydride. When placed over quicklime in a desiccator, they lose the whole of their acetic anhydride but retain their water, so that the anhydride is not combined with the water in the form of acetic acid. Copper sulphate yields the *compound* $CuSO_4,H_2O,Ac_2O$. Nickel sulphate yields the *compound* $NiSO_4,H_2O,2Ac_2O$, which on placing in a desiccator over quicklime loses only 1 mol. of acetic anhydride, leaving the *compound* $NiSO_4,H_2O,Ac_2O$. Magnesium sulphate yields the *compound* $MgSO_4,1{\cdot}3H_2O,2Ac_2O$ which also loses only 1 mol. of acetic anhydride by the action of quicklime. J. W. B.

Salts of *iso*Valeric Acid and α-Bromo*iso*valeric Acid with Organic Bases. H. GOLDSCHMIDT and O. NEUSS (D.R.-P. 386616; from *Chem. Zentr.*, 1924, i, 1713).—It is claimed that neutral salts of diethylenediamine with *iso*valeric acid and α-bromo-*iso*valeric acid may be prepared. *Diethylenediamine* isovalerate has m. p. 136°. *Diethylenediamine* α-*bromo*isovalerate sinters at 136° and decomposes at higher temperatures. G. W. R.

Synthesis of Normal Fatty Acids from Stearic Acid to Hexacosanoic Acid. P. A. LEVENE and F. A. TAYLOR (*J. Biol. Chem.*, 1924, **59**, 905—921).—The syntheses were carried out by the series of reactions: $R{\cdot}CO_2R \rightarrow R{\cdot}CH_2{\cdot}OH \rightarrow R{\cdot}CH_2I \rightarrow R{\cdot}CH_2{\cdot}CN \rightarrow R{\cdot}CH_2{\cdot}CO_2H$. The following compounds are recorded: Ethyl stearate, m. p. 32·5—33·5°; b. p. 152°/0·18 mm. *Ethyl* n-*nonadecoate*, m. p. 37—38°; b. p. 166—

168°/0·27 mm. *Ethyl* n-*eicosoate*, m. p. 41·5—42·5°; b. p. 177°/0·28 mm. *Ethyl* n-*heneicosoate*, m. p. 45—46°. *Ethyl* n-*docosoate*, m. p. 48·5—49·5°; b. p. 184—185°/0·20 mm. *Ethyl* n-*tricosoate*, m. p. 52—53°; b. p. 198—199°/0·27 mm. *Ethyl* n-*tetracosoate*, m. p. 55·5—56·5°; b. p. 198—199°/0·24 mm. *Ethyl* n-*pentacosoate*, m. p. 58—59°; b. p. 216—217°/0·50 mm. Methyl stearate, m. p. 38·5—39·5°. *Methyl* n-*nonadecoate*, m. p. 39·5—40·5°. *Methyl* n-*eicosoate*, m. p. 46—47°. *Methyl* n-*heneicosoate*, m. p. 48—49°. *Methyl* n-*docosanoate*, m. p. 53—54°. *Methyl* n-*tricosoate*, m. p. 55—56°. *Methyl* n-*tetracosoate*, m. p. 59—60°. *Methyl* n-*pentacosoate*, m. p. 61—62°. n-*Nonadecanol*, m. p. 62—63°; b. p. 166—167°/0·32 mm. n-*Eicosanol*, m. p. 65·5—66·5°; b. p. 178°/0·40 mm. n-*Heneicosanol*, m. p. 68—69°. n-*Docosanol*, m. p. 70·5—71·5°; b. p. 180°/0·22 mm. n-*Tricosanol*, m. p. 73·5—74·5°; b. p. 191—193°/0·7 mm. n-*Tetracosanol*, m. p. 76·5—77·5°; b. p. 210—210·5°/0·40 mm. n-*Pentacosanol*, m. p. 78·5—79·5°; b. p. 214—216°/0·36 mm. n-*Octadecyl iodide*, m. p. 34·5—35·5°; b. p. 164°/0·22 mm. n-*Nonadecyl iodide*, m. p. 42·5—43·5°; b. p. 174—174·5°/0·22 mm. n-*Eicosyl iodide*, m. p. 42—43°. n-*Heneicosyl iodide*, m. p. 49—50°. n-*Docosyl iodide*, m. p. 48·5—49·5°; b. p. 198°/0·23 mm. n-*Tricosyl iodide*, m. p. 55—56°; b. p. 205°/0·45 mm. n-*Tetracosyl iodide*, m. p. 54·5—55·5°; b. p. 207—209°/0·35 mm. n-*Pentacosyl iodide*, m. p. 60—61°. n-*Octadecyl cyanide*, m. p. 42·5—43·5°. n-*Nonadecyl cyanide*, m. p. 49·5—50·5°. n-*Eicosyl cyanide*, m. p. 48·5—49·5°. n-*Heneicosyl cyanide*, m. p. 55·5—56·5°. n-*Docosyl cyanide*, m. p. 53·5—54·5°. n-*Tricosyl cyanide*, m. p. 61—62°. *n*-Tetracosyl cyanide, m. p. 58—59°. n-*Pentacosyl cyanide*, m. p. 61—62°. Stearic acid, m. p. 70·5—71·5°. n-*Nonadecoic acid*, m. p. 69—70°. n-*Eicosanoic acid*, m. p. 76—77°. n-*Heneicosoic acid*, m. p. 75—76°. *n*-Docosoic (behenic) acid, m. p. 81—82°. n-*Tricosoic acid*, m. p. 80—81°. n-*Tetracosoic acid*, m. p. 85—86°. n-*Pentacosoic acid*, m. p. 84—85°. n-*Hexacosoic acid*, m. p. 88—89°. C. R. H.

Action of Alcoholic Iodine Solutions on Unsaturated Fatty Acids and Fatty Oils. Influence of Water and Potassium Iodide on the Course of the Reaction. B. M. Margosches, W. Hinner, and L. Friedmann (*Ber.*, 1924, **57**, [*B*], 996—1001; cf. this vol., i, 487).—The action of alcoholic iodine solutions on oleic acid is not confined to the alcoholic solution, but proceeds, especially if the period of reaction is short, after diluting the mixture with water preparatory to titrating the excess of iodine; the addition of hypoiodous acid is apparently almost instantaneous at the moment of dilution. The presence of potassium iodide hinders the reaction, probably on account of its tendency to reverse the reaction: $I_2+H_2O \longrightarrow I(OH)+HI$ (cf. also Ingle, A., 1902, i, 528; 1904, ii, 456). Experiments in which the addition of water was omitted, or its influence restricted by the prior addition of carbon tetrachloride, gave lower iodine values after 1 hour's contact with the iodine solution, and it thus appears that the quickening of the reaction is due to the water itself. Similar results were obtained

with castor, sesamé, poppy-seed, and linseed oils in alcoholic solution. The free acid liberated in these experiments corresponds with about 50% of the iodine consumed, except in the case of castor oil, when it amounts to 60—65%. R. B.

Autoxidation of Fats. G. R. Greenbank and G. E. Holm (*Ind. Eng. Chem.*, 1924, **16**, 598—601).—The presence of water and water vapour seems to retard the autoxidation of fats, and to a greater or less extent the formation of those compounds that are responsible for the tallowy odour. Fatty acids act probably indirectly as catalysts for autoxidation, through the liberation of unsaturated acids (especially oleic acid) which are strongly catalytic in this reaction. The resistance of butter fat to autoxidation may be increased by thorough washing of the fat or by passing steam through it, but prolonged heating or steam treatment has the opposite effect. The results of experiments at 95° on the rate of absorption of oxygen by butter fat in the dry condition and mixed with water, oleic acid, and butyric acid, respectively, are given graphically. The addition of water increases the period of induction before the absorption of oxygen begins. Once the absorption commences, the shape of the curves is almost identical whether fatty acid or water is present or not. The presence of free fatty acids decreases the period of induction, oleic acid being more effective in this respect than butyric acid. H. C. R.

I. Oxidation of Sodium Lactate by Hydrogen Peroxide. II. Effect of Cystine and Glycine on the Oxidation of Sodium Lactate by Hydrogen Peroxide. G. B. Ray (*J. Gen. Physiol.*, 1924, **6**, 509—523, 525—529).—I.—The reaction between hydrogen peroxide and sodium lactate was studied by observing the rate of production of carbon dioxide and by titrating the amount of peroxide present at various stages. In the early stages of the reaction there was found an increased amount of peroxide when the experiment was performed in the presence of air, but not in its absence. In the latter case, the end-product of the reaction was acetaldehyde. From these results and from the observations on the carbon dioxide production, the author concludes that the reaction is of an auto-catalytic type and that the increased peroxide observed in the presence of air is due to the formation of acetyl peroxide from the acetaldehyde which is the first product of reaction. Ferric chloride increases the production of carbon dioxide if added to the peroxide solution first, but inhibits it if added first to the sodium lactate.

II.—The rate of production of carbon dioxide in the reaction above described is augmented considerably by the presence of cystine and slightly by glycine. Since it is influenced by the presence of the sulphydryl group, the process is probably one of dehydrogenation. C. R. H.

Aliphatic Hydroxy-acids. I. M. Asano (*J. Pharm. Soc. Japan*, 1924, No. 504, 75—86).—Heptoyl chloride was converted into ethyl heptoylacetoacetate from which the acetyl group was removed with ammonia and the product reduced with sodium

amalgam to β-hydroxypelargonic acid, m. p. 59—60°. *Ethyl hydrogen azelate*, b. p. 169—170°/2 mm., 178°/4 mm., 193°/9 mm., m. p. 26—27°, was prepared by heating a mixture of azelaic acid (1 mol.) and anhydrous ethyl alcohol (2·5 mols.) or a mixture of ethyl azelate (1 mol.) and water (2·5 mols.) in a sealed tube at 150° during 6 hours. The yields in both the methods do not exceed 50%, but no resinous substance is produced. Ethyl hydrogen pimelate, b. p. 166°/5 mm., 155°/2 mm., is prepared by the same method. By the action of zinc propyl iodide on ethyl azelayl chloride, *ω-butyroyloctoic acid*, $C_3H_7{\cdot}CO{\cdot}[CH_2]_7{\cdot}CO_2H$, m. p. 56°, is produced; *semicarbazone*, m. p. 131°. A small amount of *αη-dibutyroylheptane*, $(C_3H_7{\cdot}CO)_2[CH_2]_7$, m. p. 71°, was produced as a by-product; the *disemicarbazone* melts at 166°. The conversion of the ketonic acid into its chloride did not proceed smoothly.

K. K.

Influence of the Base on the Degree of Conversion of Primary Salts of Dibasic Acids in Aqueous Solution. T. Sabalitschka and G. Kubisch (*Z. anorg. Chem.*, 1924, **134**, 79—86).—The authors have determined the acid content of ethereal extracts of aqueous solutions of the primary salts of camphoric, oxalic, succinic, fumaric, and maleic acids with potassium, sodium, lithium, ammonium, aniline, carbamide, and benzamide. For the primary camphorates, oxalates, succinates, and fumarates of potassium, sodium, lithium, and ammonium, similar amounts of free acid pass into the ethereal layer. In some cases, *e.g.*, in the case of benzamide oxalate and maleate, the ether dissolves some of the salt. The greater free acid content of the ether in the case of the primary salts of aniline, carbamide, and benzamide than in that of alkali and ammonium salts is conditioned by hydrolytic decomposition. The relation of acid transference, aniline salt < carbamide < benzamide, is for aniline and carbamide in agreement with the known dissociation constants. Camphoric and fumaric acids liberated from the primary alkali and ammonium salts pass completely into the ethereal layer, succinic acid less completely, and oxalic and maleic acids only very slightly. The conversion of the acid salt depends on the distribution of the free acid between ether and water and the ratio of the dissociation constant of both hydrogen atoms. The degree of conversion of the acid salt to normal salt and free acid in aqueous solution is for the individual salts of that acid the same so long as the salt undergoes no appreciable hydrolytic decomposition. The degree of decomposition is independent of the base so long as it is sufficiently strong to give salts which are not appreciably hydrolysed. J. B. F.

Syntheses using Sodamide. XII. Action of Ethyl Chloroformate on the Sodium Compounds of certain Ketones. A. Haller and E. Bauer (*Ann. Chim.*, 1924, [x], **1**, 275—297).—After treatment with sodamide, phenyl *iso*propyl ketone interacts with ethyl chloroformate to yield chiefly *α-phenyl-β-methyl-Δ$^{\alpha}$-propenyl ethyl carbonate*, $CMe_2{:}CPh{\cdot}O{\cdot}CO_2Et$, m. p. 41—42°, b. p. about 135°/10 mm.; the product is hydrolysed to the original ketone,

gives no oxime, and generally is quite different from its isomeric *C*-derivative, ethyl α-benzoyl*iso*butyrate (Blaise and Courtot, A., 1906, i, 794). When the *oxime* of the latter (needles, m. p. 135—136°) is subjected to hydrolysis, or prepared directly in alkaline solution, it is converted into 3-phenyl-4 : 4-dimethyl*iso*oxazolone, m. p. 70—71°. The sodium compound of phenyl ethyl ketone and ethyl chloroformate produces two compounds, viz., *α-phenyl-Δ$^{\alpha}$-propenyl ethyl carbonate*, b. p. 140—145°/11—12 mm., and the *ethyl carbonic* ester of *ethyl β-hydroxy-α-methylcinnamate*, $CO_2Et{\cdot}O{\cdot}CPh{:}CMe{\cdot}CO_2Et$, b. p. 182—185°/11 mm., which, on hydrolysis, affords ethyl α-benzoylpropionate (Perkin and Calman, T., 1886, **49**, 156); this interacts with hydroxylamine in alkaline solution to form 3-phenyl-4-methyl*iso*oxazolone, needles, m. p. 123—124°. From phenyl propyl ketone are similarly obtained *α-phenyl-Δ$^{\alpha}$-butenyl ethyl carbonate*, b. p. 143°/10 mm., and the *ethyl carbonic* ester of *ethyl β-hydroxy-α-ethylcinnamate*, m. p. 35°, b. p. 183—184°/10 mm., which yields, when hydrolysed, *ethyl α-benzoylbutyrate*. The *oxime* of the latter forms scales or needles, m. p. 80—81°; Hantzsch and Miolati's product (A., 1893, i, 583), m. p. 90—91°, is 3-phenyl-4-ethyl*iso*oxazolone, not the simple oxime. Acetophenone, treated with sodamide followed by ethyl chloroformate, yields ethyl benzoylmalonate (Bernhard, A., 1895, i, 93), a *compound*, $C_{11}H_{14}O_4$, b. p. 128—129°/11 mm., and the ethyl carbonic ester of ethyl β-hydroxycinnamate (Bernhard, *loc. cit.*). Di*iso*propyl ketone similarly yields chiefly *ethyl βδ-dimethyl-Δ$^{\beta}$-pentenyl carbonate*,

$$CHMe_2{\cdot}C(O{\cdot}CO_2Et){:}CMe_2,$$

b. p. 86°/15 mm., whilst pentamethylacetone, from the above *iso*butyrone, sodamide, and methyl iodide, gives *ethyl βδδ-trimethyl-Δ$^{\beta}$-γ-pentenyl carbonate*, b. p. 104—107°/24—25 mm. *cyclo*Hexanone, by similar treatment, is converted into a mixture of Δ^{1}-cyclo*hexenyl ethyl carbonate*, b. p. 108—110°/20 mm., and bis*cyclo*hexenehexanone (Wallach, A., 1897, i, 160). W. A. S.

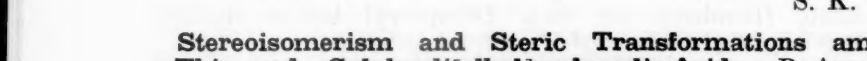
Bismuth Oxalates. E. Moles and R. Portillo (*Anal. Fis. Quím.*, 1924, **22**, 187—197; cf. this vol., i, 9).—According to the method of preparation, bismuth oxalate monohydrate is obtained with colours varying from brick-red to pink. The velocity with which water is absorbed on exposure in a moist atmosphere differs with the colour of the monohydrate. The red monohydrate absorbs water more quickly than the pink monohydrate, and when dried over sulphuric acid loses 3 of the 6 mols. of water thus absorbed, whilst in the case of the pink monohydrate 5 mols. of water are taken up, of which 3 are lost on drying over sulphuric acid. It is supposed that the single molecule of water in the monohydrate is more closely associated with the nucleus than the molecules which are absorbed from a moist atmosphere. Four hydrates are mentioned containing, respectively, 6, 5, 3, and 2 mols. of water in addition to the single molecule associated with the nucleus. G. W. R.

Thermal Decomposition of Calcium Oxalate. E. Moles and C. Díaz Villamil (*Anal. Fis. Quím.*, 1924, **22**, 174—186).—When traces of moisture are present, the initial temperature of

decomposition of anhydrous calcium oxalate is 380°; carbon monoxide and carbon dioxide are evolved together with water vapour, and the residue of calcium carbonate is grey in colour and contains carbon and traces of formic acid. Using perfectly dry anhydrous calcium oxalate, the decomposition also begins at 380°, and is represented by the equation, $CaC_2O_4 \rightleftharpoons CaCO_3+CO$. The decomposition is thus incomplete and the residue contains calcium oxalate. At higher temperatures (470—480°), the decomposition is represented by the equation $7CaC_2O_4=7CaCO_3+5CO+CO_2+C$.

G. W. R.

Reaction between Antimony Pentachloride and Ethyl Oxalate. P. Pfeiffer (*Z. anorg. Chem.*, 1924, **133**, 101—106).—The behaviour of antimony pentachloride towards *o*-hydroxyketones is exactly analogous to that of stannic chloride (A., 1913, i, 879). Two mols. of the ketone combine with 1 mol. of the halide and, on warming, 1 mol. of ketone and 1 mol. of hydrogen chloride are eliminated. Thus β-acetyl-α-naphthol reacts to give *β-acetyl-α-naphthoxy-antimony tetrachloride*, $Ac\cdot C_{10}H_6\cdot O\cdot SbCl_4$. Ethyl oxalate behaves similarly (cf. A., 1902, i, 358):



S. K. T.

Stereoisomerism and Steric Transformations among α-Thio- and α-Sulpho-di[alkyl]carboxylic Acids. R. Ahlberg (*J. pr. Chem.*, 1924, [ii], **107**, 241—329; cf. Lovén and Ahlberg, A., 1921, i, 223; Loven, A., 1908, i, 714, and earlier papers).—Sodium α-bromobutyrate and sodium sulphide interact in aqueous solution to give almost equimolecular proportions of *meso*-α-thiodibutyric acid, $S(CHEt\cdot CO_2H)_2$, m. p. 109° (Lovén, *loc. cit.*), and the *racemic* isomeride, m. p. 82°. The *potassium hydrogen* salt is described. The acid is resolved with the help of the active phenylethylamines. l-*Phenylethylammonium* l-*thiodibutyrate*, m. p. 142—143°, $[\alpha]_D$ −46·0°, and d-*phenylethylammonium* d-*thiodibutyrate*, $[\alpha]_D$ +43·6°, are described. l-α-*Thiodibutyric acid* forms prisms, m. p. 35°, $[\alpha]_D$ −152°; the *d*-variety has $[\alpha]_D$ +145°. Slow racemisation takes place in aqueous solution at 100°. The normal *silver*, *potassium hydrogen*, and d-*phenylethylammonium hydrogen* meso-α-*thiodibutyrates* were prepared. In preparing the α-thiodi*iso*valeric acid, it was found better to treat ethyl α-bromo*iso*valerate with alcoholic sodium sulphide; the crude *ethyl* α-*thiodi*i*sovalerate* obtained had b. p. 165—168°/17 mm. It was hydrolysed and converted into the strychnine salt, which, fractionally crystallised, gave *meso*-α-thiodi*iso*valeric acid, m. p. 136° (cf. Lovén, *loc. cit.*), and small quantities of the *racemic* variety. The latter is also obtained by heating the *meso*-form at 200—210°, and in considerable proportion when the *diethyl* ester (b. p. 160—162°/13 mm.) of the latter is hydrolysed. The *potassium*, *sodium*, *magnesium*, *barium*, *calcium*, *strontium*, *copper*, *silver*, *strychnine*, *brucine*, and l-α-*phenylethylammonium* salts of *meso*-α-thiodi*iso*valeric acid were prepared.

The *ethyl* ester has b. p. 160—162°/13 mm. The *potassium hydrogen*, *potassium sodium*, *magnesium*, *barium*, *copper*, and *silver* salts of the *r*-acid are described. The acid is resolved into optically active components by means of *l*-phenylethylamine or brucine. d-α-*Thiodiisovaleric acid* has m. p. 80·5—81°, $[\alpha]_D$ +129°; the *lævo isomeride* has m. p. 81—81·5° and $[\alpha]_D$ −126·5°. The brucine salts were isolated. The solubilities of all these acids and of many of their salts are recorded, and also the affinity constants, from conductivity measurements, for the acids. It is shown that, for the series α-thiodiacetic acid–α-thiodi*iso*valeric acid, the racemic form in every case is the stronger acid, whilst the optical activity (for the three acids possessing the property) decreases with rise in molecular weight for the acids, but increases for their salts. *meso*-α-Thiodibutyric acid oxidised with alkaline permanganate yields the sulphone, *r*-α-sulphodibutyric acid (Lovén, *loc. cit.*); *l*-α-thiodibutyric acid similarly oxidised gives a lævorotatory product which, even in cold aqueous solution, rapidly loses its optical activity and the same product as from the inactive thio acid can be isolated. Optically active acids were, nevertheless, isolated from the brucine salts of the racemic sulphone acid, but rapid racemisation prevented their characterisation in any other way than by the optical activity of the solutions; d-α-*sulphodibutyric acid* crystallises but has no definite m. p. The *potassium hydrogen* salt of the meso variety is described. *r*-α-Thiodi*iso*valeric acid carefully oxidised with alkaline permanganate gives r-α-*sulphoxydiisovaleric* acid, m. p. 152—152·5°. The *meso*-thio acid, further oxidised, yields a little of this, together with a mixture of *racemic* (Lovén, *loc. cit.*) and meso-α-*sulphodiisovaleric acids*, m. p. 131—133°; the *sodium*, *potassium*, *magnesium*, *zinc*, *calcium*, *barium*, *cinchonine*, *brucine*, and *strychnine* salts are described. The *potassium hydrogen* and *barium* salts of the corresponding *r*-acid were prepared. Oxidation of the optically active α-thiodi*iso*valeric acids yields optically active products which rapidly racemise, but they can be isolated by fractionally crystallising the brucine and cinchonine salts of the racemic variety. The brucine salt of l-α-*sulphodiisovaleric* acid has m. p. 139° and the free acid $[\alpha]_D$ −30·6°; the cinchonine salt of the *d*-variety (decomp. 115°) similarly gives an acid, $[\alpha]_D$ +30·2°. Both rapidly racemise in warm aqueous solution. The author discusses at length the mechanism of the racemisation and the conversion of the meso into the racemic forms. The reactions are unimolecular and evidently depend on enolisation, either through the carboxy or the sulpho group, or both. W. A. S.

"Alcoholic Fermentation" of Formaldehyde by Osmium. II. E. Müller (*Z. physikal. Chem.*, 1923, **107**, 347—356; cf. A., 1922, i, 110).—Osmium catalyses the reduction of formaldehyde to methyl alcohol only when present in the colloidal or highly dispersed condition. The metal is obtained in this condition by adding to the formaldehyde an osmium compound, such as osmic acid, which is then reduced to the metal in a highly active form. An examination of the catalytic reaction at 100° shows that the

gas evolved is not entirely carbon dioxide as the equation $3H{\cdot}CHO+H_2O=CO_2+2CH_3{\cdot}OH$ demands, but contains hydrogen and methane in addition, and sometimes, although in very small quantities, carbon monoxide. The formation of hydrogen and methane is due to the changes, $H{\cdot}CHO+H_2O=2H_2+CO_2$ and $2H{\cdot}CHO=CH_4+CO_2$. Experiments show that an increasing evolution of methane is accompanied by a decreasing evolution of hydrogen and that as the ratio, volume of aldehyde solution : weight of osmium, increases the amount of methane formed decreases, the reaction producing the alcohol always predominating. The time taken for the catalytic action and the gas evolution to reach a maximum is increased by increasing p_H, and the magnitude of the maximum is reduced. The induction period before the catalytic action begins appears to be the same whether the formaldehyde is heated with the osmium compound or kept cold, and the catalysis differs little whether the osmium is added in the form of the tetroxide, potassium osmate, or potassium chloro-osmate. The volume relations of the gases evolved are about the same in all cases, and when the reaction is concluded the osmium is present in the colloidal condition. The similarity between the present reaction and fermentation by yeast is pointed out. J. F. S.

Formaldehyde. H. von Wartenberg, A. Muchlinski, and G. Riedler (*Z. angew. Chem.*, 1924, **37**, 457—459).—The heat of combustion of formaldehyde and its polymerides has been redetermined as follows: $CH_2O_{gas}+O_2=CO_2+H_2O_{liq.}+15{\cdot}88\pm0{\cdot}033$ Cal.; $CH_2O_{para}+O_2=CO_2+H_2O_{liq.}+12{\cdot}21\pm0{\cdot}0085$ Cal.; $\frac{1}{3}(CH_2O)_3+O_2=CO_2+H_2O_{liq.}+10{\cdot}95\pm0{\cdot}007$ Cal. From this it follows that the heat of transformation of formaldehyde into paraformaldehyde and α-trioxymethylene is as follows: $CH_2O_{gas}\longrightarrow CH_2O_{para}+36{\cdot}7$ Cal. $\longrightarrow \frac{1}{3}(CH_2O)_3+1{\cdot}26$ Cal. and the heat of formation of gaseous formaldehyde from its elements is $C_{diamond}+\frac{1}{2}O_2+H_2=CH_2O_{gas}+4{\cdot}0\pm0{\cdot}3$ Cal. Attempts to synthesise formaldehyde by subjecting mixtures of carbon monoxide and hydrogen to the silent electric discharge at pressures up to 30 atms. gave only the merest trace of the substance. A mixture of carbonyl chloride with 15 times its volume of hydrogen yielded 3·6% of the theoretical amount of formaldehyde when passed over nickelised pumice at 300°. A maximum yield of 2% of formaldehyde based on the methane content of a mixture of methane and ozone was obtained when the mixture was passed over silver or lead chromate at 650°; at higher temperatures the yield rapidly fell to zero. A. R. P.

Rate of Oxidation of Aldehydes. M. Seijoo (*Anal. Asoc. Quím. Argentina*, 1923, **11**, 151—171).—Data are given for the velocity of oxidation of formaldehyde, acetaldehyde, and benzaldehyde, respectively, by potassium permanganate and sulphuric acid. The reaction is found to be unimolecular when very dilute solutions of potassium permanganate are used. G. W. R.

Tautomerism of Ethyl Acetoacetate and Acetylacetone. Absorption Spectra of These and Related Compounds. P. Grossmann (*Z. physikal. Chem.*, 1924, **109**, 305—352).—The pro-

portion present of the enolic form of ethyl acetoacetate and acetylacetone in various solvents, both pure and mixed in varying proportions, has been determined by titration with bromine and by quantitative absorption spectra measurements. The proportion found may vary slightly with concentration even for very dilute solutions, but no explanation of this is suggested. The velocity of the isomeric change was studied in various solvents, but in spite of careful purification, the reaction proved too susceptible to catalytic influence for reproducible results. In several cases, determinations were made at 0° and 25° and the heats of reaction calculated, but these varied with the solvent. Alkaline solutions were studied by a slight modification of the usual practice. Instead of acidifying the solution before treating with bromine, with consequent ketisation, acid bromine solution was added direct and excess bromine removed by aniline hydrochloride. Results were confirmed by spectroscopic measurements. Excess of alkali favours the enolic form. Similar results were obtained with acetylacetone. With still greater excess of alkali, the results are even higher, corresponding with the presence of a dienol. Analogous results are afforded by acetylacetone.

On warming alkaline solutions of ethyl acetoacetate, ketonic fission takes place, but, in the cold, hydrolysis occurs slowly and quantitatively. The course of hydrolysis was followed simultaneously with the proportion present of the enolic form. The resulting solution of sodium acetoacetate is only 0·2% enolic if the ester and alkali are mixed in equivalent proportions, but with excess alkali this is increased and, in great excess of alkali, may attain 5%. In spite of the complication of formation of enol, the reaction is bimolecular. Acetylacetone hydrolyses to acetone and sodium acetate quantitatively: the reaction corresponds with the simultaneous hydrolysis of the ketonic and enolic (and perhaps the dienolic) forms at different rates. In both cases, the conductivity scarcely alters during hydrolysis, so the enolic forms must be ionised about as highly as sodium acetate, and complex formation is excluded.

The ultra-violet absorption spectra of ethyl acetoacetate and acetylacetone and other substances of similar composition in various solvents are given quantitatively. That of ethyl acetoacetate in the vapour state at room temperature was also studied and found closely to resemble that of the pure liquid. It is deduced that 5% must be in the enolic form. A ring structure in the gaseous state is excluded, as the band is continuous and cannot be resolved into the fine lines characteristic of unsaturated ring compounds.

L. J. H.

Keto-enolic Desmotropy. III. Determination of Enols by Titration with Thiocyanogen. H. P. KAUFMANN and G. WOLFF (*Ber.*, 1924, **57**, [*B*], 934—937).—Experiments with ethyl acetoacetate, acetyldibenzoylmethane, ethyl diacetylsuccinate, and ethyl formylphenylacetate show that the equilibrium of keto-enolic desmotropes can be determined by titration with thiocyanogen if the rate of transformation is sufficiently slow; nitromethane is particularly suitable as a solvent. From the points of view of

convenience and general applicability, the method is inferior to Meyer's bromine titration method. H. W.

Compounds of Quadrivalent Nickel with Dimethylglyoxime. F. FEIGL.—(See ii, 504.)

Colour Reaction between Cobalt Salts and Dimethylglyoxime in the Presence of Sulphides. F. FEIGL and L. VON TUSTANOWSKA.—(See ii, 504.)

Oxidation of Carbohydrates with Air. H. A. SPOEHR (*J. Amer. Chem. Soc.*, 1924, **46**, 1494—1502).—Methylene-blue is reduced by dextrose in solutions containing disodium phosphate, the rate of reduction being proportional to the concentration of the latter from 0·025 to 0·75*M*, and to that of the dextrose from 0·05 to 0·5*M*. On drawing a stream of air through the solution, the blue colour is restored and carbon dioxide formed. Lævulose reacts similarly, from five to eight times as rapidly as dextrose. The rate of production of carbon dioxide is increased threefold by the addition of a trace of a solution of ferric phosphate in sodium citrate ("soluble ferric phosphate"). The methylene-blue is gradually consumed, possibly on account of production of hydrogen peroxide. Sodium ferropyrophosphate, $Na_8Fe_2(P_2O_7)_3$, catalyses the above reaction, and also brings about atmospheric oxidation of dextrose alone, the rate of formation of carbon dioxide first increasing rapidly and then slowly diminishing. Sodium ferripyrophosphate, $Na_6Fe_2(P_2O_7)_3$, is less active, and sodium manganopyrophosphate shows only about 0·1% of the activity of iron. Prior aëration of the catalyst has no effect on its activity. Maximum oxidation was attained at p_H 7·2. *d*-Mannose, *d*-galactose, sucrose, trehalose, and mannitol are also oxidised in presence of sodium ferropyrophosphate, disodium phosphate, and potassium dihydrogen phosphate, the oxidation of sucrose also proceeding in solution of p_H 6·8. Evidence of hydrolysis of sucrose and trehalose prior to oxidation was not obtained. The oxidation of dextrose is probably accompanied by partial conversion into lævulose and ketoses, and some formation of saccharic acid.

F. G. W.

Behaviour of Sugars in Dilute Alkaline Solutions. I. Cause of the Transformation of Dextrose in Dilute Solutions of Potassium Hydroxide. J. GROOT (*Biochem. Z.*, 1924, **146**, 72—90).—The lowering of rotation of dextrose solutions of various concentrations from 0·16*M* to 0·66*M*, in the presence of potassium hydroxide varying between 0·05*N* and 1·0*N* has been studied quantitatively. For various concentrations of dextrose the extent to which the rotation is lowered increases with increasing hydroxide concentration, the limiting value being about 2/9 of the rotation of the original dextrose solution at equivalent dilution. For any given concentration of dextrose the velocity of the decrease in rotation increases with increasing hydroxide concentration, until a limiting value is reached beyond which further increases in the hydroxide concentration produce no effect on the velocity of the change of rotation. The latter attains its maximum when the ratio of dextrose to potassium hydroxide is unimolecular, and this is independent of

the original dextrose concentration. The results resemble the de Bruyn–van Ekenstein transformation and are interpreted as representing the conversion of dextrose into a mixture of this and other hexoses which proceeds as a unimolecular reaction, the following equation being deduced as applying within the limits between which K varies with N: $K = 12{\cdot}8M/N$ (at 25°), where K=velocity constant with a maximum value of 12·8, M=molar concentration of dextrose, and N=normality of the potassium hydroxide. In a theoretical discussion of the results the view is expressed that the cause of the changes observed is the formation of potassium glucosate, $C_6H_{11}O_6K$, and the instability of this compound in aqueous solution. J. P.

Fluoro-acetyl Derivatives of Sugars. III. Optical Rotation and Atomic Dimension. D. H. Brauns (*J. Amer. Chem. Soc.*, 1924, **46**, 1484—1488).—*Fluorotriacetyl*-l-*arabinose* forms brilliant needles, m. p. 117—118°, $[\alpha]_D^{20}$ +138·18° in chloroform. Chlorotriacetyl-*l*-arabinose has $[\alpha]_D^{20}$ +244·32° (cf. Chavanne, A., 1902, i, 346; Ryan and Mills, T., 1901, **79**, 706), and bromotriacetyl-*l*-arabinose has m. p. 138—139°, $[\alpha]_D^{20}$ +287·11° (cf. Chavanne, *loc. cit.*). *Iodotriacetyl*-l-*arabinose*, prepared similarly to iodo-tetra-acetylglucose (E. and H. Fischer, A., 1910, i, 716), forms colourless crystals, $[\alpha]_D^{20}$ +339·06°. The differences in specific rotations of the above compounds are approximately proportional to the differences in atomic diameters of the halogen atoms, and are in agreement with similar relationships previously found for analogous derivatives of other carbohydrates. F. G. W.

Halogen Compounds of Starch. M. Bergmann and S. Ludewig (*Ber.*, 1924, **57**, [*B*], 961—963).—Starch acetates, obtained by short treatment of starch with a saturated solution of hydrogen chloride in acetic anhydride at 0°, retain the typical affinity of starch towards mixtures of iodine and potassium iodide and the power of absorbing bromine, thus lending support to the authors' view (this vol., i, 618) that the formation of halogen compounds is attributable to certain bridge oxygen atoms of starch. H. W.

Alkoxyl Groups of the Wood and Lignin of the Pine. E. Hägglund and B. Sundroos (*Biochem. Z.*, 1924, **146**, 221—225).—From determinations of the alkoxyl content of pine wood and of the lignins prepared from it, by the Zeisel and Feist-Willstätter methods, and since the latter method yields only phenyltrimethylammonium iodide or tetramethylammonium iodide, it is concluded that the alkoxyl groups consist wholly of methoxyl. J. P.

Ammonia and Amine Compounds of Stannic Dialkyl Halides. P. Pfeiffer (*Z. anorg. Chem.*, 1924, **133**, 91—100).—Stannic dialkyl halides combine with quinoline or aniline to give crystalline additive compounds which are unstable towards heat and have indefinite melting points (cf. A., 1911, i, 747). Dry ammonia combines with stannic dialkyl halides at the ordinary temperature to form additive ammonia compounds in which the co-ordination number of the tin is probably 8 (cf. A., 1923, ii, 867).

Diquinoline stannic dimethyl chloride, $SnMe_2Cl_2,2C_9H_7N$, forms white crystals, m. p. 40—60°, unstable in moist air; the corresponding *bromide*, m. p. 80—115°, behaves similarly. *Dianiline stannic dimethyl chloride*, $SnMe_2Cl_2,2PhNH_2$, when dissolved in pyridine, yields the corresponding pyridine compound; the *iodide* forms unstable, pale yellow crystals. *Dianiline stannic diethyl chloride* and the *bromide*, $SnEt_2X_2,2PhNH_2$, *monoaniline stannic diethyl bromide* and *dianiline stannic dipropyl bromide* were also prepared.

The *ammonia* compounds, $SnR_2X_2,4NH_3$, were prepared, where R=Me, X=Cl, Br and I; R=Et, X=Br and I; R=Pr, X=Cl and Br. The compound with R=Et and X=Cl contained only $3NH_3$. S. K. T.

Organic Silver Complexes. F. G. Pawelka (*Z. Elektrochem.*, 1924, **30**, 180—186).—By the use of the method described by Bödlander, the complexity of a number of additive derivatives of organic substances and silver nitrate has been determined. If the complexes are considered to be of the general type, $[Ag_mR_n](NO_3)_m$, then $m=1$ and $n/m=2$ in the case of the following silver derivatives: sodium thiosulphate, dimethylamine, diethylamine, triethylamine, hexamethylenetetramine, glycine, acetonitrile, propionitrile, ethylene cyanide, and toluidine. In the case of thiocarbamide, $m=1$ and $n/m=3$. H. T.

Preparation of *p*-Aminobenzoyl Derivatives of δ-Methyl-β-dimethyl(diethyl)aminopentan-α-ol. Chemische Fabrik Flora (Brit. Pat. 200810).—δ-Methyl-β-dimethyl(diethyl)aminopentan-α-ol (cf. Karrer and others, this vol., i, 168) is converted into the *p*-nitrobenzoic ester and the latter is reduced. *δ-Methyl-β-diethylaminoamyl* p-*nitrobenzoate hydrochloride*, m. p. 163°, and *δ-methyl-β-diethylaminoamyl* p-*aminobenzoate hydrochloride*, m. p. 190°, are described. The latter substance has valuable therapeutic properties. W. T. K. B.

Mixed Crystals, consisting of 2 Mols. of Glycine, or 2 Mols. of Alanine, or 1 Mol. of Glycine and 1 Mol. of Alanine, combined with 1 Mol. of Hydrochloric Acid. E. Abderhalden and H. Sickel (*Z. physiol. Chem.*, 1924, **135**, 29—31).—From the strongly acidified mother-liquors of a tyrosine preparation the authors isolated crystals of *glycinealanine monohydrochloride*, rectangular needles, m. p. 177° after softening at 105°, $[\alpha]_D^{19}$ +4·42°. Recrystallisation from water gave rhombic crystals of *diglycine monohydrochloride*, m. p. 178°. The crystals, together with *dialanine monohydrochloride*, m. p. 214°, $[\alpha]_D^{21}$ +9·13°, were also prepared directly from the amino-acids and hydrochloric acid by slow evaporation. E. M. C.

Action of Sulphuric Acid on some Amino-acids and on the Vinasse from the Distillation of Molasses. P. G. Kronacker (*Bull. Soc. chim. Belg.*, 1924, **33**, 217—231).—Determinations have been made of the proportions of nitrogen convertible into ammonium sulphate by the action of sulphuric acid on various amino-acids known to be present in sugar juices. The whole of the nitrogen in glycine, asparagine, aspartic acid, glutamic acid, and leucine

was converted by treatment with sulphuric acid (66%). In the case of betaine it was necessary to use 95% acid with permanganate or mercury. It is suggested that dehydration causes betaine to form a stable ring compound. On treatment with 66% acid, tryptophan gave a low result which is ascribed to the formation of a stable tautomeric form; the theoretical value was obtained when the Stolzenberg–Kjeldahl method was used. Arginine gave a low result when treated with 66% acid. F. B.

Sulphamic Ester and its Isomerisation to Compounds of the Betaine Type. W. TRAUBE, H. ZANDER, and H. GAFFRON (*Ber.*, 1924, **57**, [*B*], 1045—1051).—An attempt to prepare methyl sulphamate by the action of diazomethane on the acid led to the production of a *substance*, m. p. 239°, which is also obtained, in 93% yield, by the action of methyl iodide on dry silver sulphamate at the ordinary temperature. On account of its difference in properties from the dimethylsulphamic esters prepared by Behrend (A., 1884, 285), the constitution, $\overline{\text{NMe}_3\cdot\text{SO}_2\cdot\text{O}}$, is ascribed to the substance, which is thus *anhydrotrimethylsulphamic acid*. The isomeric *methyl dimethylsulphamate*, pale or yellow oil, obtained by the action of sodium methoxide on dimethylsulphamyl chloride, undergoes conversion into the trimethylsulphamic acid even at the ordinary temperature, and is probably produced intermediately in the formation of trimethylsulphamic acid. The reaction with silver sulphamate proceeds according to the equation $3\text{NH}_2\cdot\text{SO}_3\text{Ag}+3\text{MeI}=\overline{\text{NMe}_3\cdot\text{SO}_2\cdot\text{O}}+2\text{NH}_2\cdot\text{SO}_3\text{H}+3\text{AgI}$, two-thirds of the silver sulphamate being found as free sulphamic acid. The course of this reaction depends on the weight of the alkyl radical participating. Thus with ethyl iodide the product is *ethyl diethylsulphamate*, $\text{NEt}_2\cdot\text{SO}_3\text{Et}$, in 80% of the theoretical yield, whilst with benzyl chloride in chloroform solution the product is *benzyl benzylsulphamate*, m. p. 90°. R. B.

Determination of the Constitution of the Eutectic Mixture of Methyl, Ethyl, and *iso*Butyl Oxamates. A. PRAETORIUS (*Z. anal. Chem.*, 1924, **64**, 96—102).—By thermal analysis, the results of which are plotted on a triangular diagram, the eutectic mixture, m. p. 56°, of methyl, ethyl, and *iso*butyl oxamates was found to consist of 16·5% of the methyl, 24·5% of the ethyl, and 59% of the *iso*butyl ester. The error in calculating the result from the analytical figures for carbon and nitrogen amounted to 10%. A. R. P.

Chlorides of Thiocyanogen. H. P. KAUFMANN and J. LIEPE (*Ber.*, 1924, **57**, [*B*], 923—928).—Thiocyanogen dissolved in cold chloroform reacts with chlorine in three ways, yielding, respectively, *thiocyanogen monochloride*, (SCN)Cl, sulphur chloride and cyanuric chloride, and *thiocyanogen trichloride*, $(\text{SCN})\text{Cl}_3$. The monochloride crystallises in colourless needles which become yellow at about 150° and darken, without melting, at a higher

temperature. It is comparatively stable towards water, by which it is ultimately hydrolysed to sulphur, hydrocyanic, hydrochloric, thiocyanic, and sulphuric acids. The trichloride, which is more conveniently prepared in ethyl bromide solution, is a yellow liquid with a very unpleasant odour, b. p. 54—56°/20 mm., 152—153°/760 mm. It is slowly decomposed by cold water into sulphur, thiocyanic, hydrocyanic, hydrochloric, and sulphuric acids and by sodium hydroxide solution (10%) into hydrocyanic, thiocyanic, hydrochloric, sulphurous, thiosulphuric, and sulphuric acids, hydrogen sulphide, carbon dioxide, and ammonia. H. W.

Titrations with Free Thiocyanogen. H. P. KAUFMANN and P. GAERTNER (*Ber.*, 1924, **57**, [*B*], 928—934).—Solutions of thiocyanogen in organic media can be accurately titrated by agitation with at least twice the equivalent quantity of potassium iodide dissolved in water and determination of the liberated iodine. In cases in which the end-point is obscured by the separation of thiocyano compounds, alcoholic sodium iodide solution may replace aqueous potassium iodide. The application of thiocyanogen in volumetric analysis is restricted by the necessity of using anhydrous solvents and dry vessels to avoid hydrolysis, and by the limited stability of such solutions owing to the tendency towards polymerisation. With a sufficient excess of sodium thiosulphate or hydrogen sulphide, respectively, thiocyanogen reacts quantitatively according to the equations $2Na_2S_2O_3+(CNS)_2=2NaSCN+Na_2S_4O_6$ and $(SCN)_2+S''=2SCN'+S$. In carbon tetrachloride solution, antipyrine reacts rapidly and quantitatively with an excess of thiocyanogen, whereas α- and β-naphthols react similarly, but more slowly. Thymol dissolved in nitromethane is moderately rapidly transformed into 4-*thiocyano*-6-iso*propyl*-m-*cresol*, yellow needles, m. p. 108—109°. H. W.

Thiocyanatocobaltous Acid and its Alkali Salts. F. J. ALLEN and A. R. MIDDLETON (*Proc. Indiana Acad. Sci.*, 1922, 153—158).—Experiments on the partition of sulphuric acid, thiocyanic acid, and cobalt between water and a 1 : 4-mixture of ethyl alcohol and ethyl ether showed the ether layer to contain equivalent proportions of cobalt and thiocyanate, and larger amounts of thiocyanic acid, but practically no cobalt thiocyanate or potassium thiocyanate; they do not elucidate the composition of the blue compounds obtained by Rosenheim and Cohn (A., 1901, i, 455), which probably consist of one or more complex acids, $H_{2x}Co(SCN)_{4x}$, containing cobalt in the anion. Both the blue complex alkali thiocyanatocobaltites and the purple compound, $Co(SCN)_2,3H_2O$, can be prepared by double decomposition in aqueous solution from cobalt sulphate, the alkali sulphate being removed with ethyl alcohol, thus avoiding the use of unstable thiocyanic acid. The form of the compounds, $K_2Co(SCN)_4$ and $(NH_4)_2Co(SCN)_4$ stable in air is the trihydrate (cf. Treadwell, A., 1901, ii, 284). The purple salt, $Co(SCN)_2,3H_2O$, on exposure to warm air, yields the yellowish-brown hemihydrate. CHEMICAL ABSTRACTS.

Double Salt of Zinc and Cæsium Ferricyanides. I. M. KOLTHOFF and E. J. A. H. VERZIJL (*Rec. trav. chim.*, 1924, **43**, 394—396).—In the potentiometric titration of a zinc salt with potassium ferrocyanide containing a little ferricyanide, addition of cæsium chloride causes a considerable fall in the potential of the electrode (cf. this vol., ii, 501). This is due to the formation of a very sparingly soluble *zinc cæsium ferricyanide*,

$$2Zn_3[Fe(CN)_6]_2,Cs_3Fe(CN)_6,$$

the precipitation of which increases the ratio ferrocyanide : ferricyanide on which the electrode potential depends. E. H. R.

Addition of Mono- and Poly-hydric Alcohols and Mercaptans to Azodicarboxylic Ester. O. DIELS and C. WULFF (*Annalen*, 1924, **437**, 309—318; cf. A., 1922, i, 774, 1194; 1923, i, 391; this vol., i, 673).—Azodicarboxylic ester reacts with alcohols and mercaptans with varying velocity, yielding additive compounds of 1 mol. of alcohol with 1 mol. of ester (2 mols. of ester in the case of glycols). In the presence of potassium acetate the additive compounds are decomposed, yielding nitrogen, hydrazo ester, and the alkyl carbonate. Methyl alcohol and methylazodicarboxylate yield the colourless *additive* compound,

$$CO_2Me\cdot N(OMe)\cdot NH\cdot CO_2Me,$$

a colourless, viscous oil, d_4^{20} 1·3024; $n_{H\alpha}^{20}$ 1·44475, n_D^{20} 1·44887. Similarly, ethyl alcohol and methyl azodicarboxylate yield the *compound*, $CO_2Me\cdot N(OEt)\cdot NH\cdot CO_2Me$, a bright, viscous, highly refracting oil, decomposing on distillation into nitrogen, hydrazo ester, and methyl ethyl carbonate. *iso*Butyl alcohol in 4—6 weeks yields the *compound*, $C_8H_{16}O_5N_2$, and amyl alcohol in 8 weeks the compound, $C_9H_{18}O_5N_2$, colourless, viscous, highly refracting oils. With ethyl mercaptan, methyl azodicarboxylate yields in 24 hours the *compound*, $C_6H_{12}O_4N_2S$, a thick, colourless oil, d_4^{20} 1·2537, $n_{H\alpha}^{20}$ 1·48330, $n_{H\beta}^{20}$ 1·49410, which with fuming hydrochloric acid is decomposed into nitrogen, methyl hydrazodicarboxylate, and ethyl disulphide. Ethylene glycol and methyl azodicarboxylate in cold ethereal solution in the presence of a little potassium acetate yield in 2—3 days a little dimethyl ethylene dicarbonate, and the *additive* compound, $C_{10}H_{18}O_{10}N_4$, d_4^{20} 1·3296, $n_{H\alpha}^{20}$ 1·44918, $n_{H\beta}^{20}$ 1·45734, which dissociates in acetone yielding ethylene carbonate and hydrazo ester, whilst with potassium acetate reaction takes place, yielding nitrogen, methyl hydrazodicarboxylate, and *dimethyl ethylene dicarbonate*, $(CH_2\cdot O\cdot CO_2Me)_2$, ester-like oil, b. p. 215—220°/760 mm., which on boiling in ether yields ethylene and dimethyl carbonates. R. B.

Catalytic Decomposition of Hexahydro-aromatic and Saturated Aliphatic Hydrocarbons. The Cracking of Petroleum. V. GRIGNARD and R. STRATFORD (*Compt. rend.*, 1924, **178**, 2149—2152).—The effect of aluminium chloride as a catalyst in the cracking of hydrocarbons was studied at temperatures between 120° and 150°, the proportion of catalyst used being 20—30%. *cyclo*Hexane and methyl*cyclo*hexane remained unchanged, whilst *o*-dimethyl- and, less readily, *p*-dimethyl-*cyclo*-

hexane were transformed into the *m*-compound. With derivatives having a side-chain of 2 or 3 carbon atoms, branched or not, about 1—5% was cracked, giving a saturated aliphatic hydrocarbon and polymerised *cyclo*hexene, the remainder forming polymethyl*cyclo*hexanes with the methyl groups in the meta positions to each other. *m*-Diethyl*cyclo*hexane was chiefly converted into tetramethyl*cyclo*hexane with some butane. The three butyl*cyclo*hexanes were cracked to the extent of 13—15%, the normal and secondary compounds producing *n*-butane, the tertiary, a mixture of butanes. The uncracked portion gave tetramethyl*cyclo*hexanes. Amyl- and *iso*amyl-*cyclo*hexanes decompose to the extent of 70% and 42%, respectively, into methyl*cyclo*hexane and butane, the rest isomerising to tetra- and penta-methyl*cyclo*hexanes. *n*-Octane, $\beta\zeta$-dimethylhexane, *n*-decane, $\beta\eta$-dimethyloctane, and heptadecane all gave *n*-butane, the longer chains being broken at both ends simultaneously. A. COUSEN.

0 : 1 : 3-*dicyclo*Hexane. N. ZELINSKY and M. OUCHAKOFF (*Bull. Soc. chim.*, 1924, [iv], **35**, 484—487).—0 : 1 : 3-*dicyclo*Hexane, $CH_2<\begin{matrix}CH_2\cdot CH\\ CH_2\cdot CH\end{matrix}>CH_2$, the simplest example of a combined three- and five-membered ring, is prepared by reduction, with sodium and alcohol, of ethyl 2-keto*cyclo*pentanecarboxylate to the corresponding glycol. The dibromide is formed by heating the latter under pressure with phosphorus tribromide at 100°, and by treatment with zinc powder gives dicyclo*hexane*, b. p. 78—79·5°/745 mm. It is not affected by bromine. A. B. H.

X-Ray Diffraction Patterns from Crystalline and Liquid Benzene. E. D. EASTMAN.—(See ii, 448.)

Sulphonation of *m*-Dinitrobenzene. R. H. GRIFFITH (*J. Chem. Soc.*, 1924, **125**, 1401—1402).—The direct sulphonation of *m*-dinitrobenzene with fuming sulphuric acid (18% SO_3) at 150—160° in the presence of mercury yields 3 : 5-dinitrobenzenesulphonic acid (A., 1903, i, 407) in 38% of the theoretical yield. The product is sensitive to alkali, and apparently changes readily to a nitrohydroxybenzenesulphonic acid. R. B.

***s*-Tribromobenzyl Chloride and some of its Transformations.** M. HENRAUT (*Bull. Soc. chim. Belg.*, 1924, **33**, 132—138).—Addition of benzyl chloride and bromine to anhydrous aluminium bromide yields 2 : 4 : 6-*tribromobenzyl chloride*, yellow crystals, m. p. 153—154°, which when oxidised by nitric acid under pressure is converted into 2 : 4 : 6-tribromobenzoic acid. The chloride reacts with potassium cyanide to form 2 : 4 : 6-*tribromophenylacetonitrile*, a brown solid, m. p. 138—139°, which on hydrolysis at 150° with alcoholic potassium hydroxide affords 2 : 4 : 6-*tribromophenylacetic acid*, m. p. 157—158°, of which the *chloride* and the *amide*, m. p. 162—163°, were prepared. H. J. E.

Polarity Effects in Aromatic Halogen Compounds. J. B. SHOESMITH, A. C. HETHERINGTON, and R. H. SLATER (*J. Chem. Soc.*, 1924, **125**, 1312—1319).—The hydrolysis of the isomeric

ω-bromotoluic acids in alcohol is in accordance with the principle of induced alternate polarities (T., 1922, **121**, 1392; 1923, **123**, 2828), the meta-isomeride being more readily hydrolysed than the para-, whilst with hydrogen iodide the para- is more readily reduced than the meta-isomeride. The behaviour of the ortho-compound is abnormal in both cases, owing to phthalide formation due to spatial influences. Since benzyl bromide is more readily hydrolysed than any of the ω-bromotoluic acids, the introduction of the carboxyl group has stabilised the molecule as a whole. The hydrolysis of the nitrobenzyl bromides follows the same rule, the *m*-isomeride being the most readily hydrolysed, but the introduction of the nitro group into a very reactive molecule such as *p*-methoxybenzyl bromide diminishes the reactivity of the latter to the order of that of the unsubstituted compound. 3-Nitro-4-hydroxybenzyl bromide is more readily hydrolysed by aqueous alcohol than 3-nitro-4-methoxybenzyl bromide. The order of reduction of the halogenated phenols with hydriodic acid in acetic acid solution: *p*-iodo > *o*-iodo > *p*-bromo > *o*-bromo > *p*-chloro, is also in accordance with the theory. The *m*-isomerides showed no tendency to be reduced, and of the chlorophenols only the *p*-compound showed any reduction. *ω-Bromo-p-toluoyl bromide*, b. p. 160—165°/14 mm., m. p. 39—40°, prepared by Davies and Perkin's method (T., 1922, **121**, 2202), yields ω-bromo-*p*-toluic acid, m. p. 223° (Zalkind, A., 1914, i, 957), on warming with formic acid. ω-Bromo-*m*-toluoyl bromide has b. p. 160—165°/14 mm., m. p. 23—25°. *o-Nitrobenzyl bromide*, light yellow plates, m. p. 45·5°, was obtained from *o*-nitrobenzyl chloride and phosphorus pentabromide. *3-Nitro-4-hydroxybenzyl bromide*, yellow, prismatic needles, m. p. 82°, was obtained from dry hydrogen bromide and the alcohol in benzene solution. *3-Nitro-4-methoxybenzyl bromide*, pale yellow needles, m. p. 108°, was similarly obtained from 3-nitro-4-methoxybenzyl alcohol. *m*-Bromophenol distils at 125—127°/12 mm. (cf. Diels and Bunzl, A., 1905, i, 431). R. B.

Solubility of 2 : 4 : 6-Trinitrotoluene, "Tetryl," and Tetranitroaniline in Organic Solvents. L. Desvergnes (*Mon. Sci.*, 1924, **14**, 121—130).—A detailed *résumé* of previous work by Taylor and Rinkenbach is given (A., 1923, i, 315, 320, 672). The solubility of 2 : 4 : 6-trinitrotoluene in 95% alcohol is 1·26 at 15°, 20·45 at 78·5°, and of trinitrophenylmethylnitroamine (tetryl) in water, 0·007 at 15°, 0·017 at 30°, 0·020 at 50°, 0·051 at 80°, 0·116 g. at 100°, per 100 g. of solvent in each case. A. C.

Specific Heats of Trinitrotoluene, "Tetryl," Picric Acid, and their Molecular Complexes. C. A. Taylor and W. H. Rinkenbach (*J. Amer. Chem. Soc.*, 1924, **46**, 1504—1510).—The following specific heats were determined by means of the Dewar liquid oxygen calorimeter, using lead as the standard of comparison. Tetryl, 0°, 0·213; 125°, 0·235; picric acid, 0°, 0·234; 120°, 0·337; trinitrotoluene, 0°, 0·309; 80°, 0·374; tetryl–picric acid compound, 0°, 0·254; 80°, 0·311; tetryl–trinitrotoluene compound, 0°, 0·287; 60°, 0·349. Intermediate specific heats

are tabulated at 10° intervals, and equations deduced for the temperature–mean specific heat curves from −182·8° to the highest temperature used for each substance. Kopp's law does not hold for trinitrotoluene, "tetryl," or picric acid. F. G. W.

Specific Heat and Thermal Diffusivity of certain Explosives. III. A. M. Prentiss (*Army Ordnance*, 1924, **4**, 242—246; cf. *ibid.*, 1923, **4**, 184).—For trinitrotoluene, trinitroxylene, and trinitrophenylmethylnitroamine, respectively, the specific heats are: 0·3776 (−200° to +50°), 0·3950 (+20° to 50°), 0·4233 (+20° to 50°); the coefficients of conductivity at 25° are: 0·00043, 0·00057, 0·00088, and the coefficients of diffusivity at 25°, 0·00197, 0·00225, and 0·00388, respectively. Chemical Abstracts.

Derivatives of Tetrahydro- and Decahydro-naphthalenes. E. Bœdtker and O. Rambech (*Bull. Soc. chim.*, 1924, [iv], **35**, 631—638).—The authors confirm the observation of Schroeter (D.R.-P. 333158) that aluminium chloride reacts with tetrahydronaphthalene at the ordinary temperature with formation of benzene and octahydro-anthracene and -phenanthrene, and demonstrate that the reaction is reversible. Methyltetrahydronaphthalene could not be obtained by the Friedel–Crafts reaction, but tetrahydro-2-ethylnaphthalene (b. p. 244°) was obtained in small yield. 2-iso*Propyltetrahydronaphthalene*, b. p. 255—256°, d_4^{16} 0·9518, n_D^1 1·5352, is obtained similarly from *n*-propyl chloride and tetrahydronaphthalene. The formation of 2-tert.-*butyltetrahydronaphthalene*, b. p. 265·5—266·5°, d_4^{15} 0·9463, n_D^{15} 1·5348, is accompanied by evolution of *iso*butane. 2-tert.-*Amyltetrahydronaphthalene* has b. p. 149·2—150°/12 mm., d_4^{17} 0·9478, n_D^{17} 1·5332, b. p. 280°/760 mm., with partial decomposition. When decahydronaphthalene is boiled with aluminium chloride, a mixture of saturated hydrocarbons, $C_{10}H_{18}$, b. p. 157—250°, is obtained.

F. G. W.

Bromine Compounds of Phenanthrene. III. H. Henstock (*J. Chem. Soc.*, 1924, **125**, 1296—1299).—The bromination of potassium phenanthrene-2-sulphonate in aqueous solution yields a product giving a brilliant dark green *barium* salt, which in the absence of ammonium chloride changes almost instantaneously to a brown powder, normal *barium* 10-*bromo*-9-*hydroxyphenanthrene*-2-*sulphonate*. The green barium salt on acidifying with hydrochloric acid yields an *acid*, $C_{14}H_8OBr{\cdot}SO_3H$, bright blue, amorphous powder, which is much more stable than the salt and probably possesses the constitution: $\begin{matrix} C_6H_4{\cdot}CO \\ | \\ SO_3H{\cdot}C_6H_3{\cdot}CHBr \end{matrix}$. With dry bromine vapour, potassium phenanthrene-2-sulphonate is converted into an orange-yellow *dibromide*, $C_{14}H_9Br_2{\cdot}SO_3K$, fuming in air through loss of hydrogen bromide, which on heating yields the yellow *potassium* 10-*bromo*-9-*hydroxyphenanthrene*-2-*sulphonate*. The free *acid*, granular, white powder, obtained from the *silver* salt, yields a colourless, doubly-refracting jelly with concentrated hydrochloric acid, and the bromine is therefore in position 10 (cf. Sandqvist, A., 1919, i, 120; 1920, i, 300). *Sodium, ferric, ammonium, basic*

barium, $C_{14}H_7(OH)Br{\cdot}SO_3Ba(OH)$, *normal* and *basic lead* salts, $[C_{14}H_7(OH)BrSO_3]_8Pb_3$, are described. 9 : 10-*Dibromophenanthrene-2-sulphonyl bromide*, yellow, amorphous powder, has m. p. 204°. The scarlet substance previously obtained by treating 2 : 10-dibromophenanthrene with alcoholic potassium hydroxide (T., 1921, **119**, 59) has the composition $C_{28}H_{14}O_2Br_2$, yields *p*-bromodiphenic acid, m. p. 237—238° (cf. Schmidt and Junghans, A., 1904, i, 1033) on oxidation, and probably has the constitution

$$\begin{array}{l} C_6H_4{\cdot}CO\ CO{\cdot}C_6H_4 \\ BrC_6H_3{\cdot}C{=}C{-}C_6H_3Br \end{array}$$

R. B.

Space Lattice of Triphenylmethane. K. Becker; H. Mark and K. Weissenberg.—(See ii, 449.)

Triphenylmethyl Fluoride. F. F. Blicke (*J. Amer. Chem. Soc.*, 1924, **46**, 1515—1518).—*Triphenylmethyl fluoride*, m. p. 102—104°, was obtained by the action of acetyl fluoride on triphenylcarbinol suspended in benzene. It is much less reactive than the corresponding compounds of the other halogens, remaining unaffected after shaking for 24 hours in benzene solution, with 10 mols. of molecular silver, mercury, zinc, copper, bronze, or magnesium, and on boiling with excess of silver in benzene for 6 hours in an atmosphere of nitrogen. It is reduced by zinc chloride in ether, and oxidised by potassium permanganate in acetone, with quantitative formation of triphenylmethane and triphenylcarbinol, respectively. It condenses slowly with amines, and with magnesium phenyl bromide yields triphenylmethyl, triphenylcarbinol, and a red oil, but no tetraphenylmethane. F. G. W.

Action of Formaldehyde on Formylated Aromatic Amines and on Isatin. A. Reissert and A. Händeler (*Ber.*, 1924, **57**, [*B*], 989—996).—Formanilide is slowly converted by formaldehyde in aqueous alkaline solution into formic acid, and *formylmethylenedianiline*, $CHO{\cdot}NPh{\cdot}CH_2{\cdot}NHPh$, m. p. 93°, the constitution of which is established by its reduction with sodium amalgam to aniline, methylaniline, and formic acid; the *benzoyl* derivative has m. p. 119°. Boiling, aqueous potassium cyanide solution transforms formylmethylenedianiline into aniline, *anilinoacetamide*, m. p. 141°, anilinoacetic acid, and *anilinodiaceticmonoamide*, $CO_2H{\cdot}CH_2{\cdot}NPh{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, m. p. 217°. *Formylmethylenedi-o-toluidine* has m. p. 108—109° (*benzoyl* derivative, m. p. 130°). *Formylmethylenedi-p-toluidine* has m. p. 92—93° (*benzoyl* derivative, m. p. 120—121°).

1-*Hydroxymethylisatin*, red crystals, m. p. 156—157°, is the main product of the interaction of equimolecular proportions of isatin and formaldehyde in boiling aqueous solution. The *oxime*, reddish-yellow needles, m. p. 138° (decomp.), *phenylhydrazone*, m. p. 180—181°, *acetate*, m. p. 112—113°, and *benzoate*, m. p. 124—125°, are described. *Methylenedi-isatin*, $\left[CO\left<\begin{matrix}CO\\C_6H_4\end{matrix}\right>N\right]_2CH_2$, a yellow, crystalline powder, decomp. 287° [*dioxime*, m. p. 230—231° (decomp.); *monophenylhydrazone*, decomp. 289—290°] is obtained as a by-product in the preparation of 1-hydroxymethylisatin. Isatic

acid is converted by ice-cold formaldehyde solution into "*methylene-di-isatin hydrate*," $C_{17}H_{12}O_5N_2$, decomp. 262—264°, after darkening at 230°, the constitution of which has not been elucidated. It yields a *monoxime*, m. p. 208°, and is converted by boiling methyl alcohol into methylenedi-isatin. H. W.

Action of Potassium Cyanide on Aromatic Mustard Oils. A. REISSERT and K. BRÜGGEMANN (*Ber.*, 1924, **57**, [*B*], 981—989). —An extension of previous work (Reissert, A., 1904, i, 990).

Thio-oxanilonitrile is converted by benzoyl chloride and sodium carbonate into the corresponding N-*benzoyl* derivative, NPhBz·CS·CN, red needles, m. p. 103°, which is mixed with the *amide*, yellow needles, m. p. 218°, if sodium hydroxide is substituted for the carbonate. *Methylthio-oxanilonitrile* is a viscous, orange-coloured liquid, b. p. 160°/23 mm., from which methylaniline is obtained by the action of alkalis. Thio-oxanilothioamide, m. p. 98°, is readily prepared by the action of yellow ammonium sulphide on thio-oxanilonitrile. The latter substance is transformed by ethyl alcohol and hydrogen chloride in the presence of an inert solvent into *ethyl imidothio-oxanilate*, NHPh·CS·C:NH(OEt), yellow needles, m. p. 73°; the corresponding *hydrochloride*, m. p. 166°, is converted by alcohol into ethyl thio-oxanilate, m. p. 38—40°. Thio-oxanilonitrile is converted by aniline in boiling benzene into *phenylimido-oxanilonitrile*, NHPh·C(CN):NPh, m. p. 137°, the yield being poor. *Thio-oxalo*-o-*toluidinonitrile*, C_7H_7·NH·CS·CN, orange-coloured needles, m. p. 64°, is converted into the corresponding *benzoyl* derivative, m. p. 103°, the *amide*, yellow needles, m. p. 117°, and the *thioamide*, pale red needles, m. p. 90°. *Thio-oxalo*-p-*toluidinonitrile*, yellow needles, m. p. 127—128°, is converted by the methods used with the phenyl compound into the *benzoyl* derivative, m. p. 123°, *amide*, m. p. 169°, *thioamide*, m. p. 128°, *ethyl imidothio-oxalo*-p-*toluidinate*, C_7H_7·NH·CS·C:NH(OEt), m. p. 73° (*hydrochloride*, m. p. 166—167°), *ethyl thio-oxalo*-p-*toluidinate*, m. p. 82°, and *thio-oxalo*-p-*toluidinic acid*, m. p. 130°. *Thio-oxalo*-m-*xylidinonitrile*, yellow needles, m. p. 98°, yields the corresponding *amide*, m. p. 147°, *thioamide*, m. p. 136°, and *benzoyl* derivative, m. p. 104°. *Thio-oxalo*-α-*naphthylaminonitrile*, pale red needles, m. p. 136°, gives rise to the corresponding *amide*, m. p. 199°, and *thioamide*, m. p. 147°; the *benzoyl* derivative, red needles, m. p. 135°, is converted by exposure to sunlight into the colourless *dimeride*, m. p. 165—166°. *Thio-oxalo*-β-*naphthylaminonitrile* crystallises in yellow needles, m. p. 157°.

The action of hydrogen peroxide on the thionitriles leads mainly to the production of derivatives of oxamide. The thioamides are converted by potassium ferricyanide into thiazole derivatives, of which the following are described: 3-*methylbenzthiazole*-1-*carboxylamide*, m. p. 163°, and the corresponding *acid*, m. p. 110—111°; 5-*methylbenzthiazole*-1-*carboxylamide*, m. p. 243°, the corresponding *acid*, m. p. 110—111° (decomp.), and its *silver* salt and *methyl* ester, m. p. 96°; 3 : 5-*dimethylbenzthiazole*-1-*carboxylamide*, m. p. 192°,

and the corresponding *acid*, m. p. 114°; *α-naphththiazole-1-carboxylamide*, m. p. 210°, and *α-naphththiazole-1-carboxylic acid*, m. p. 129—130°. H. W.

Salts of Phenyldiguanidine. E. ROMANI (*Caoutchouc et Gutta-Percha*, 1923, **20**, 12005—12008).—An investigation of the utility of derivatives of guanidine as accelerators for the vulcanisation of caoutchouc. *α-Phenyldiguanidine carbonate*, R_2,H_2CO_3 [where R=NH:C(NHPh)·NH·C(NH$_2$):NH], has m. p. 128—130°; *carbamide*, m. p. 216—218°; *hydrosulphide*, R,H_2S, m. p. 155°; *polysulphide*, R_2,H_2S_2, m. p. 209—210°; *thiocyanate*, R,HSCN, nacreous, m. p. 232°; *thiocarbamide*, m. p. 142—143°. *Phenyldiguanidinoethylthiocarbamide* has m. p. 246°; *phenyldiguanidinophenylthiocarbamide* was prepared. *Phenyldiguanidine dithiocarbamate* has m. p. 106°; *dithiophenylcarbazinate*, m. p. 142°; *piperidyldithiocarbamate*, m. p. 94—95°; *phenyldithiocarbamate*, m. p. 140°; *ethylxanthate*, pale yellow, m. p. 128°; *dithiopyromucate*, garnet red, m. p. 158°; *mercaptobenzthiazole* compound, yellow, m. p. 160; *zincate* (cf. Cohn, A., 1911, i, 928).

CHEMICAL ABSTRACTS.

Action of Carbon Dioxide on Phenoxides. H. MEYER (*Z. anal. Chem.*, 1924, **64**, 72—81).—The passage of carbon dioxide through solutions of alkali phenoxides at 0° produces crystalline precipitates consisting of definite compounds of the free phenol with the alkali phenoxide. Some of these substances may be purified by recrystallisation from organic solvents whilst others are decomposed in these media into the phenol which dissolves and the alkali phenoxide which remains insoluble. The following compounds have been prepared: PhOK,3PhOH, long, thin, colourless needles, m. p. 114°; *p*-C_6H_4Me·OK,3*p*-Me·C_6H_4·OH, m. p. 148°; *o*-NO_2·C_6H_4·OK,*o*-NO_2·C_6H_4·OH,3H_2O, golden-yellow leaflets, *o*-NO_2·C_6H_4·ONa,*o*-NO_2·C_6H_4·OH,6H_2O, red crystals, and

o-NO_2·C_6H_4·ONH_4,*o*-NO_2·C_6H_4·OH,H_2O,

yellowish-brown leaflets; *m*-NO_2·C_6H_4·OK,2*m*-NO_2·C_6H_4·OH,5H_2O, brown crystals decomposed on warming;

p-NO_2·C_6H_4·OK,*p*-NO_2·C_6H_4·OH,3H_2O,

short, thick, ochre-yellow needles, m. p. 170° (decomp.),

2*p*-NO_2·C_6H_4·ONa,3*p*-NO_2·C_6H_4·OH,3H_2O,

thick, brownish-yellow needles, m. p. 156° (decomp.),

p-NO_2·C_6H_4·ONH_4,*p*-NO_2·C_6H_4·OH,H_2O,

small yellow leaflets, m. p. 126—130° (decomp.); from 3-nitro-*p*-cresol, NO_2·C_7H_6·OK,5NO_2·C_7H_6·OH,8H_2O, reddish-brown crystals, m. p. 53°, NO_2·C_7H_6·ONa,7NO_2·C_7H_6·OH,8H_2O,

NO_2·C_7H_6·ONH_4,2NO_2·C_7H_6·OH,4H_2O,

yellow powder, m. p. 140° (decomp.);

α-$C_{10}H_7$·OK,4α-$C_{10}H_7$·OH,5H_2O,

green, amorphous powder; β-$C_{10}H_7$·OK,2β-$C_{10}H_7$·OH,5H_2O, colourless crystals; from pyrocatechol, OH·C_6H_4·OK,$C_6H_4(OH)_2$,2H_2O, colourless crystals, 2OH·C_6H_4·ONa,$C_6H_4(OH)_2$,6H_2O, colourless, glistening crystals; from quinol, colourless crystals,

OH·C_6H_4·OK,7$C_6H_4(OH)_2$

and $OH\cdot C_6H_4\cdot ONa,4C_6H_4(OH)_2$; from guaiacol,
$OMe\cdot C_6H_4\cdot OK,OMe\cdot C_6H_4\cdot OH,1{\cdot}5H_2O$,
large colourless needles, m. p. 186° (decomp.),
$2OMe\cdot C_6H_4\cdot ONa,5OMe\cdot C_6H_4\cdot OH,2H_2O$,
colourless crystals, m. p. 139°; from 4-nitroguaiacol,
$OMe\cdot C_6H_3(NO_2)OK,OMe\cdot C_6H_3(NO_2)\cdot OH,3H_2O$,
yellow crystals, m. p. 169—171°; from 5-chloroguaiacol,
$OMe\cdot C_6H_3Cl\cdot OK,OMe\cdot C_6H_3Cl\cdot OH,2H_2O$,
yellowish-white, very stable needles, m. p. 146°. In purifying phenols by the carbon dioxide method, the substance should be dissolved in sodium hydroxide and the gas passed through the warm solution for a prolonged period to avoid contamination of the precipitate by complex compounds. A. R. P.

Sulphonation of *m*-Cresol and its Methyl Ether. R. D. Haworth and A. Lapworth (*J. Chem. Soc.*, 1924, **125**, 1299—1307; cf. T., 1923, **123**, 2982).—The sulphonation of *m*-cresol with concentrated sulphuric acid at 30—35° yields *m*-cresol-4- and -6-sulphonic acids in the ratio 1 : 2·7; the 6-sulphonic acid is also the main product at 120° (cf. Claus and Krauss, A., 1888, 280). The acids were separated by means of their barium salts and identified by methylation of the potassium salts to the corresponding 3-methoxytoluenesulphonates.

[With M. L. Wilson.]—Sulphonation with chlorosulphonic acid (1 mol.) in carbon disulphide at −15° yields potassium *m*-tolyl sulphate (Verley, A., 1901, i, 143) and potassium *m*-cresol-6-sulphonate. In the presence of pyridine, 70% of the theoretical yield of potassium *m*-tolyl sulphate was obtained. On heating the mixture at 100°, after distilling off the carbon disulphide, *m*-cresol-6-sulphonic acid alone was obtained. The *barium* (decomp. 180°), *ammonium*, *ferrous*, *zinc*, and *potassium* salts of *m*-cresol-6-sulphonic acid are described, and the *barium* (decomp. 150°), *copper*, and *potassium* salts of *m*-cresol-4-sulphonic acid. With 2 or 3 mols. of chlorosulphonic acid below 35° *m*-cresol yields *m*-cresol-4 : 6-disulphonic acid (*barium* salt), the product, after distilling off the carbon disulphide, being heated at 100° to ensure migration of the sulphonic group to the nucleus. No *m*-cresolsulphonyl chloride was produced. Sulphonation of *m*-tolyl methyl ether with chlorosulphonic acid at −15° gave only 3-methoxytoluene-6-sulphonic acid in good yield. Nitration of potassium *m*-cresol-6-sulphonate in acetic acid gives *potassium* 4-*nitro*-m-*cresol*-6-*sulphonate*, pale yellow prisms, potassium 6-nitro-*m*-cresol-4-sulphonate being similarly obtained from the 4-sulphonate. Both nitro compounds on heating with hydrochloric acid in a sealed tube yield the corresponding nitrocresol. Oxidation of potassium 3-methoxytoluene-6-sulphonate with potassium permanganate yields the *potassium hydrogen* 3-*methoxy*-6-*sulphobenzoate*, whereas oxidation of the corresponding sulphonamide yields 5-*methoxy*-o-*benzoicsulphinide*, m. p. 242°, also prepared from the potassium hydrogen salt. Potassium 3-methoxytoluene-4-sulphonate similarly yields the *potassium hydrogen* 3-*methoxy*-4-*sulphobenzoate* and 3-*methoxy*-4-*sulphamido*-

benzoic acid, m. p. 254—255°, which is also obtained by the oxidation of 3-methoxytoluene-4-sulphonamide with alkaline permanganate. 3-Methoxytoluene-2-sulphonamide similarly yields 3-*methoxy*-o-*benzoicsulphinide*, m. p. 227—228° (decomp.). R. B.

o-Hordenine [o-β-Dimethylaminoethylphenol]. J. von Braun and O. Bayer (*Ber.*, 1924, **57**, [*B*], 913—914).—Benz-*o*-β-chloroethylanilide is converted by dimethylamine in benzene solution at 100° into *benz*-o-β-*dimethylaminoethylanilide*, $NMe_2 \cdot [CH_2]_2 \cdot C_6H_4 \cdot NHBz$, m. p. 95°; the hygroscopic *hydrochloride* and the *picrate*, m. p. 160°, are described. It is hydrolysed by hydrochloric acid at 150° to o-β-*dimethylaminoethylaniline*, b. p. 129°/12 mm., m. p. 45°, which yields a very hygroscopic *hydrochloride* and a *chloroplatinate*, decomp. 209°. The base is converted through the diazonium compound into o-β-*dimethylaminoethylphenol*, a pale yellow liquid, b. p. 136—137°/13 mm., which could not be caused to crystallise; the hygroscopic *hydrochloride*, *chloroplatinate*, m. p. 144°, *sulphate*, *picrate*, m. p. 142°, and quaternary methiodide, m. p. 218°, are described. The physiological action of *o*-β-dimethylaminoethylphenol is much weaker than that of hordenine. H. W.

Catalytic Hydrogenation of *p*- and *o*-Hydroxydiphenyl. J. Ranedo and A. León (*Anal. Fís. Quím.*, 1924, **22**, 222—232; cf. A., 1923, i, 909).—Catalytic perhydrogenation of *p*-hydroxydiphenyl in presence of platinum black yields two isomerides identical with those obtained from *o-cyclo*hexylphenol by Schrauth and Görig (A., 1923, i, 1084). Perhydrogenation of *o*-hydroxydiphenyl yields a cyclo*hexyl*cyclo*hexanol* having b. p. 172—177°/75 mm., m. p. 63°. By oxidation a ketone is obtained identical with that obtained by Schrauth and Görig from the oxidation of the above isomerides. G. W. R.

Lichen Products. IV. Synthesis of Divarinol. A. Sonn and B. Scheffler (*Ber.*, 1924, **57**, [*B*], 959—961).—Methyl 3 : 5-dimethoxybenzoate is condensed with ethyl acetate and sodium to ethyl 3 : 5-dimethoxybenzoylacetate, b. p. 189—191°/28 mm., which is methylated with sodium ethoxide and methyl sulphate and then submitted to simultaneous ketonic fission and reduction by Clemmensen's method, thus yielding 3 : 5-dimethoxypropylbenzene, b. p. 147—148°/29 mm. (cf. Mauthner, this vol., i, 524). The latter substance is more readily obtained by treating the fraction of beechwood tar, b. p. 265—295°, with hot potassium hydroxide solution, whereby a mixture of the potassium salts of 5-*n*-propylpyrogallol mono- and di-methyl ethers separates. This, on methylation, gives 5-*n*-propylpyrogallol trimethyl ether, b. p. 263—265°, which is reduced by sodium and alcohol to 3 : 5-dimethoxypropylbenzene, b. p. 145—147°/27 mm. The latter substance is converted by hydriodic acid (*d* 1·7) into divarinol. Myristicin is also converted by sodium and alcohol into divarinol. The introduction of the aldehydic group into divarinol by Gattermann's method gives a *substance*, b. p. 184—185°. H. W.

Effect of Temperature and of Medium in the Dehydration of α-Phenylethyl Alcohol. R. DESCAMPS (*Bull. Soc. chim. Belg.*, 1924, **33**, 139—145; cf. Wuyts, A., 1921, i, 506).—In the dehydration of α-phenylethyl alcohol by means of *p*-toluenesulphonic acid in the absence of a solvent, the proportion of styrene obtained decreases with temperature, *e.g.*, 7·31% at 82·6°, 0·8% at 48·4°. Camphorsulphonic acid under similar conditions produces a smaller proportion of the hydrocarbon, whilst in presence of benzene as solvent the proportion is increased. In presence of carbon disulphide at 48·4°, the proportion of alcohol converted into styrene is 0·58%. The yield of ether in all the cases studied was good.

H. J. E.

Tervalent Carbon. II. Conversion of the Ethers of Tertiary Alcohols into Organic Potassium Compounds and Hexa-substituted Ethane Derivatives. K. ZIEGLER and B. SCHNELL (*Annalen*, 1924, **437**, 227—255; cf. this vol., i, 308).—The reaction of triphenylmethyl alkyl ethers with potassium (A., 1923, i, 921) has now been utilised in the conversion of tertiary ethers into hexa-substituted ethanes. Diphenylalkylcarbinols, $OH{\cdot}CPh_2R$, in cold methyl-alcoholic solution in the presence of 2% of sulphuric acid (cf. this vol., i, 509) are converted into the corresponding methyl ethers. At higher temperatures the ethers are converted into ethylene derivatives, showing that this is the final stage of the reaction. Confirmation of this conclusion is found in the fact that αα-diphenylpropylene is unchanged by methyl alcohol. With phenyldialkylcarbinols the reaction is slower and the ethers must be prepared at higher temperatures with consequent loss of yield. When the corresponding chloride is available, *e.g.*, β-phenyl*iso*propyl chloride, the ether can be obtained in good yield by the action of methyl alcohol. On shaking with potassium in cold ethereal solution, the diphenyl tertiary ethers are converted into potassium compounds: $CPh_2R{\cdot}OMe \longrightarrow CPh_2R{\cdot}K$. Phenyl tertiary ethers, *e.g.*, phenyldibenzylmethyl methyl ether, $CPh(CH_2Ph)_2{\cdot}OMe$, and β-phenyl*iso*propyl methyl ether, $CPhMe_2{\cdot}OMe$, react less readily and ethers such as *tert.*-butyl methyl ether, terpineol methyl ether, and camphene hydrate methyl ether, in which no phenyl group is attached to the tertiary carbon atom, are not attacked by potassium. On treatment with tetramethylene dibromide, these potassium compounds are decomposed, yielding hexa-substituted ethanes: $CPh_2R\ldots K \longrightarrow (\cdot CPh_2R)_2$, and in some cases the reverse reaction takes place on treating the substituted ethane with potassium. The dissociation capacity of the substituted ethanes is discussed in relation to the valency considerations advanced by Wieland, Meerwein, and Skraup.

αα-Diphenylethyl methyl ether, $CPh_2Me{\cdot}OMe$, white needles, m. p. 35—36°, yields *potassium αα-diphenylethyl*, brick-red powder, which with carbon dioxide gives 80—90% of the theoretical yield of αα-diphenylpropionic acid, and with benzyl chloride yields *αββ-triphenylpropane*, $CPh_2Me{\cdot}CH_2Ph$, dense prisms, m. p. 116—117°.

With tetramethylene dibromide in the cold, the potassium compound yields ββγγ-*tetraphenylbutane*, m. p. 126—127°. On heating, its carbon tetrachloride solution becomes unsaturated and takes up bromine, yielding ββ-diphenylvinyl bromide, in consequence of decomposition into αα-diphenylethane and αα-diphenylethylene. αα-*Diphenylpropyl methyl ether*, $CPh_2Et{\cdot}OMe$, dense, triangular plates, m. p. 68—69°, yields *potassium* αα-*diphenylpropyl*, red oil, converted into αα-diphenylbutyric acid by carbon dioxide. γγδδ-*Tetraphenylhexane*, m. p. 85—86°, obtained from this potassium compound, gradually dissociates in solution but no satisfactory reaction constant was obtained. The cold, freshly-prepared solution in carbon disulphide is saturated, but gradually becomes unsaturated and 1 mol. of bromine is taken up. ααβ-*Triphenylethyl methyl ether*, $CH_2Ph{\cdot}CPh_2{\cdot}OMe$, flat, sword-like cusps or radial prisms, m. p. 93—94°, gives *potassium* ααβ-*triphenylethyl*, small, brown crystals with blue lustre, yielding ααβ-triphenylpropionic acid (this vol., i, 171) with carbon dioxide and αββ-triphenylpropane on treatment with methyl iodide. Attempts to obtain αββγγδ-hexaphenylbutane were unsuccessful, and only resinous substances were formed, evidently mixtures of the two decomposition products ααβ-triphenylethane and ααβ-triphenylethylene. *Diphenylcyclohexylmethyl methyl ether*, $C_6H_{11}{\cdot}CPh_2{\cdot}OMe$, laminated prisms, m. p. 69—70°, yields *potassium diphenylcyclohexylmethyl*, bright red, which with alcohol is converted into diphenyl*cyclo*hexylmethane and with carbon dioxide gives *diphenylcyclohexylacetic acid*, microcrystalline powder, m. p. 202—203°. Tetramethylene dibromide converts the potassium compound into a sparingly soluble colourless *substance* which is probably ααββ-tetraphenyl-αβ-di*cyclo*hexylethane. This substance in chloroform solution readily absorbs bromine, iodine, and oxygen, yielding in the latter case a thick oil, probably a peroxide. Treatment with potassium–sodium alloy yields the original potassium diphenyl*cyclo*hexylmethyl. αββ′-*Triphenylisopropyl methyl ether*, lustrous needles, m. p. 105—106°, gives a brownish-violet *potassium* αββ′-*triphenylisopropyl*, which with carbon dioxide yields αββ′-*triphenylisobutyric acid*,

$$(PhCH_2)_2CPh{\cdot}CO_2H,$$

m. p. 125—126°, and with tetramethylene dibromide, αβγδ-tetraphenyl-βγ-dibenzylbutane, m. p. 126—127°, which shows no tendency to dissociate in solution. β-*Phenylisopropyl methyl ether*, from β-phenyl*iso*propyl chloride, colourless oil, b. p. 78°/13 mm., with an odour resembling camphor and peppermint, gives the deep red *potassium* β-*phenylisopropyl*, which with carbon dioxide yields α-phenyl*iso*butyric acid. R. B.

Thiophenols. VI. Thiophenol Ethers of Triphenylmethane and the Bathochromic Action of Alkylthiol Groups. K. Brand and O. Stallmann (*J. pr. Chem.*, 1924, [ii], **107**, 358—382).—The corresponding carbinol (A., 1921, i, 664) is reduced by zinc and acetic acid to o-*methylthioltriphenylmethane*, colourless tablets, m. p. 111°. This combines with methyl sulphate to form a *sulphonium methyl sulphate*, $CHPh_2{\cdot}C_6H_4{\cdot}SMe_2{\cdot}SO_4Me$, colourless scales,

m. p. 163°; the corresponding *iodide* is very unstable. o-*Methylthioltriphenylmethyl chloride*, formed when the carbinol is treated with ethereal hydrogen chloride, crystallises in needles, m. p. 126°, and yields unstable coloured compounds with ferric and stannic chlorides. oo′-*Dimethylthioltriphenylmethane*, m. p. 100·5°, was obtained satisfactorily by reducing the corresponding carbinol, not with zinc and acetic acid, but with alcoholic hydrogen chloride (Kaufmann, A., 1912, i, 351). The corresponding *chloride* forms fine needles, m. p. 164° (decomp.), and also yields unstable compounds with ferric and stannic chlorides. oo′o″-*Trimethylthioltriphenylcarbinol* is formed by interaction of magnesium *o*-methylthiolphenyl bromide and methyl *o*-methylthiolbenzoate; it crystallises from alcohol in prisms, m. p. 180°, but from chloroform or benzene in octahedra, m. p. 190°. It yields the corresponding *methane* derivative, m. p. about 176°, and *chloride*, colourless rods, m. p. 140° (decomp.).

p-Methylthioltriphenylcarbinol is formed together with much *pp′*-dimethylthioldiphenyl, by interaction of magnesium *p*-methylthiolphenyl bromide and benzophenone (cf. Bistrzycki and Kuba, A., 1922, i, 33). By methods analogous to those described above, the following *p*-substituted derivatives were prepared: pp′-*dimethylthioltriphenylcarbinol*, forming needles, m. p. 110—111°, and yielding a *perchlorate*, bronzy needles, m. p. 195° (decomp.), and *double chlorides* with mercuric chloride (green needles, m. p. 122°, decomposed by water) and stannic chloride (green needles, m. p. 205—207°, unstable); pp′-*dimethylthioltriphenylmethane*, needles, m. p. 63°; pp′-*dimethylthioltriphenylmethyl chloride*, m. p. 122°; pp′p″-*trimethylthioltriphenylcarbinol* (the requisite methyl *p*-methylthiolbenzoate was obtained from *p*-cyanophenyl methyl sulphide), colourless needles, m. p. 128°, yielding a *perchlorate*, bright bronze rods, m. p. 220° (decomp.), and *double* salts with mercuric chloride (bronzy-green needles, m. p. 163—165°) and stannic chloride (prisms, m. p. about 210°). The corresponding *methane* forms colourless needles, m. p. 95·5°; *chloride*, m. p. 152°. Various colour reactions of all these substances are described.

oo′-*Dimethylthioldiphenyl* was prepared by treating *o*-iodophenyl methyl sulphide with copper bronze at 200—250°; it forms feathery crystals, m. p. 158·5°. W. A. S.

Thiophenols. VII. Simple Method of preparing *p*-Methylthiol- and *pp′*-Dimethylthiol-triphenylcarbinols. K. Brand and W. Vogt (*J. pr. Chem.*, 1924, [ii], **107**, 383—390).—By reactions resembling those of Döbner's malachite-green synthesis, phenyl methyl sulphide heated with benzophenone chloride and aluminium chloride in carbon disulphide solution yields *p*-methylthioltriphenylcarbinol, and with benzotrichloride and zinc chloride, *pp′*-dimethylthioltriphenylcarbinol (cf. preceding abstract). When equimolecular proportions of phenyl methyl sulphide and benzotrichloride are used, the product is p-*methylthiolbenzophenone*, m. p. 72—73°, which yields two *oximes*, m. p. 138° and 105°, respectively.

p-Methylthioltriphenylcarbinol gives violet-red, and *pp'*-dimethylthioltriphenylcarbinol bluish-green salts with mineral acids.

W. A. S.

Action of Organo-magnesium Compounds on Nitriles. E. Ectors (*Bull. Soc. chim. Belg.*, 1924, **33**, 146—159).—Benzonitrile acts on magnesium methyl bromide with formation of acetophenone (80% yield) together with *s*-triphenylpyridine; with magnesium ethyl bromide it yields phenyl ethyl ketone, no other product being isolated. With magnesium benzyl chloride, it forms phenyl benzyl ketone, the dimeride of phenyl benzyl ketimine, and a third substance, $C_{21}H_{18}N_2$. The dimeride is shown to be 3 : 4 : 5 : 6-*tetraphenylhexahydro*-1 : 2-*diazine*, fine needles, m. p. 192°, whilst the third product proved to be 3 : 4 : 5-*triphenylpyrazoline*, m. p. 152°, *hydrochloride*, m. p. 221° (decomp.). Benzonitrile is differentiated from aliphatic compounds such as phenylacetonitrile in its action on organo-magnesium compounds by the formation of such condensation products in addition to the high yield of ketone obtained (cf. Blaise, A., 1912, i, 164). H. J. E.

Reaction Velocity of Rearrangement of Potassium Dibenzhydroxamate. G. Dougherty and L. W. Jones (*J. Amer. Chem. Soc.*, 1924, **46**, 1535—1539).—The rearrangement of potassium dibenzhydroxamate (5·5 g. per litre) under the influence of an equivalent of potassium hydroxide, at 25°, is unimolecular for the last 75% of the reaction period, and is represented by the scheme $COPh{\cdot}NK{\cdot}O{\cdot}COPh \longrightarrow COPh{\cdot}OK + COPh{\cdot}N{:}$; $COPh{\cdot}N{:} \longrightarrow NPh{:}C{:}O$. The apparent deviation during the first 25% of the reaction time is due to the hydrolysis of the dibenzhydroxamic acid to monobenzhydroxamic and benzoic acids, the consequent increase in acidity of the reaction mixture, above that required by the actual rearrangement, ceasing as the unimolecular reaction constant assumes a steady value. F. G. W.

Correlation of Additive Reactions with Tautomeric Change. III. The Cyano-imino Additive Process. E. H. Ingold (*J. Chem. Soc.*, 1924, **125**, 1319—1322).—α-Cyano-β-imino-α-phenyl-β-*o*-tolylethane on treatment with alcoholic sodium ethoxide readily undergoes degradation to phenylacetonitrile and *o*-toluonitrile: $C_7H_7{\cdot}C(:NH){\cdot}CHPh{\cdot}CN \longrightarrow CH(H)Ph{\cdot}CN + C_7H_7{\cdot}CN$, a balanced reaction resulting. Some cyanobenzyline was also obtained from the hydrochloric acid extract. Ethyl α-cyano-β-imino-β-phenylpropionate similarly yields ethyl cyanoacetate and benzonitrile, but the equilibrium between ethyl cyanoacetate and ethyl cyanoiminoglutarate is disturbed by reactions leading to ethyl α-cyano-β-iminobutyrate: $2CH_2(CN){\cdot}CO_2Et \rightleftharpoons CO_2Et{\cdot}CH_2C(:NH){\cdot}CH(CN){\cdot}CO_2Et \longrightarrow Me{\cdot}C(:NH){\cdot}CH(CN){\cdot}CO_2Et$. This reversibility of the cyano-imino additive process is in accordance with Usherwood's views of tautomeric change (T., 1923, **123**, 1717).

R. B.

Reduction Products of *o*-Nitromandelonitrile. A. Reissert and K. Hessert (*Ber.*, 1924, **57**, [*B*], 964—972).—Reinvestigation

of the substance obtained by Heller (A., 1906, i, 585) by the reduction of *o*-nitromandelonitrile and regarded by him as a compound of the quinhydrone type composed of $N(OH)_2 \cdot C_6H_4 \cdot CH(OH) \cdot CN,HCl$ and $OH \cdot NH \cdot C_6H_4 \cdot CH(OH) \cdot CN,HCl$, leads the authors to the conclusion that it is *o*-hydroxylaminomandelamide hydrochloride.

The mode of preparation and the properties of the compound are in complete harmony with Heller's description. The substance is decomposed by warm water into isatin and *anthroxanamide*, m. p. 211—212° (considered erroneously by Heller as nitrosomandelonitrile); with acetylating agents, it yields isatin and 1-acetoxyisatin in varying amount, whilst with phenylhydrazine it gives isatin-1- and -2-phenylhydrazones and 1-hydroxyisatin-3-phenylhydrazone. The formation of derivatives of 1-hydroxyisatin is completely in accord with Heller's conception of the partial reduction of the nitro group; since, however, exactly two atomic proportions of hydrogen are used, it appears reasonable to attribute their production to intermolecular oxidation, which should therefore be accompanied by the formation of dihydroxyindole as observed by Heller and Sourlis (A., 1908, i, 208), but not by the authors.

o-Hydroxylaminomandelamide hydrochloride is converted by sodium carbonate and sodium hydroxide into *isatin-2-imide*, $C_6H_4<^{CO}_{NH}>C:NH$, golden-yellow needles, m. p. 147—148° (decomp.). It is readily hydrolysed by dilute acids into isatin and ammonia, and by alkali hydroxide to isatic acid and by aniline into isatin-2-anilide. It is easily converted into *isatin-2-phenylhydrazone*, m. p. 222°, *isatin-2-semicarbazone*, m. p. 235—236°, and *isatindioxime*, m. p. 182—183° (decomp.). Treatment of *o*-hydroxylaminomandelamide or isatin-2-imide with sodium acetate and acetic anhydride gives a *diacetyl* compound, m. p. 224—225° (decomp.) after darkening at 200°, which is regarded as an isatol derivative, $C_6H_4<^{C(OAc)}_{N\text{——}}>C:NAc$ or $C_6H_4<^{C(OAc)}_{N\text{——}}>C:NAc$. It is hydrolysed in well-marked stages to a *monoacetyl* compound, m. p. 281—282° (decomp.) after darkening at 240°, which does not exhibit ketonic properties, and ultimately to isatin.

o-Hydroxylaminobenzoic acid (cf. Bamberger and Pyman, A., 1909, i, 573) is conveniently prepared by treating *o*-nitrobenzaldehyde with sodium hydrogen sulphite and potassium cyanide and subsequently warming the solution at 60°.

Cautious oxidation of Kalle's "anhydrohydroxylaminomandelic acid" (cf. Heller, *loc. cit.*) appears to lead to the formation of 1-hydroxyisatin, which, however, could be isolated only as the phenylhydrazone. H. W.

Constitution of and Method of preparing Hydroxyphenylhomocampholic Acid. A. Haller and L. Palfray (*Compt. rend.*, 1924, **178**, 1647—1652).—From dibenzoylcamphor, 1-hydroxy-2-benzoylcamphene (Forster, T., 1901, **79**, 987) was prepared and either fused with potassium hydroxide at 195—200° (yield about

30% of theory) or heated at 200—220° with alcoholic sodium hydroxide (yield about 60%) or with a mixture of acetic and hydrochloric acids (yield about 50%) or with 50% sulphuric acid; it was thus converted (cf. cyanocamphor, Haller and Weimann, A., 1907, i, 278) into benzoylcampholic acid. This also is obtained directly, together with hydroxybenzoylcamphene, by treating dibenzoylcamphor with alcoholic sodium hydroxide (2 mols.) at 200—210°. The product is identical in all respects with that obtained from methyl cyanocampholate (*loc. cit.*). When reduced with sodium amalgam, it gives phenylhydroxyhomocampholic acid, identical with Haller and Minguin's product (A., 1900, i, 452). The hydroxy group is thus again proved to be attached to the same carbon atom as the phenyl radical, not to the adjacent one, as stated by Rupe and Blechschmidt (A., 1918, i, 222).

W. A. S.

δ-Ketonic Nitriles and their Relation to Cyclic Compounds. III. E. P. Kohler and C. F. H. Allen (*J. Amer. Chem. Soc.*, 1924, **46**, 1522—1534).—Phenylacetonitrile condenses with phenyl styryl ketone in presence of sodium methoxide with formation of two stereoisomeric *γ-cyano-βγ-diphenylbutyrophenones*,

$$CN\cdot CHPh\cdot CHPh\cdot CH_2\cdot COPh \quad (I),$$

prisms, m. p. 118° (*a*), and 109° (*b*), respectively, (*b*) being converted into (*a*) on saturating a solution of the former in chloroform or carbon tetrachloride with hydrogen bromide. The *methyl* esters of the corresponding stereoisomeric *acids* form needles, m. p. 150° and 139° respectively, and are both hydrolysed to the same *γ-benzoyl-αβ-diphenylbutyric acid*, needles, m. p. 239°, which on re-esterification gives only the ester of m. p. 150°. The action of alcoholic potassium hydroxide on the nitriles (I) affords a *substance*, $C_{38}H_{31}O_2N$, microscopic needles, m. p. 257°, which is also formed together with (I) in the above condensation. On saturating a solution of either of the isomerides (I) in glacial acetic acid with hydrogen bromide, *2-keto-3 : 4 : 6-triphenyltetrahydropyridine*, needles, m. p. 173°, was obtained, and this yielded *2-hydroxy-3 : 4 : 6-triphenylpyridine*, fluorescent prisms, m. p. 263°, on treatment with sodium nitrite in glacial acetic acid. Bromination of the isomeride (*b*) in glacial acetic acid afforded *2-bromo-3 : 4 : 6-triphenylpyridine*, fluorescent needles, m. p. 110°, from which, by the action of sodium butoxide, *2-butoxy-3 : 4 : 6-triphenylpyridine*, small needles, m. p. 94°, was obtained. In chloroform, bromination yielded, together with the above product, *2-bromo-6-hydroxy-3 : 4 : 6-triphenyl-5 : 6-dihydropyridine*, colourless needles, m. p. 100° (*benzoyl* derivative, pointed rods, m. p. 137°), together with 2-bromo-3 : 4 : 6-triphenylpyridine, the latter being also formed by the action of methyl-alcoholic potassium acetate solution or hydrogen bromide in glacial acetic acid. The nitrile (*b*) when brominated in chloroform gave *γ-bromo-γ-cyano-βγ-diphenylbutyrophenone*, $CN\cdot CBrPh\cdot CHPh\cdot CH_2\cdot COPh$ (IV), in two stereoisomeric forms, plates, m. p. 172° and 131°, respectively. The latter was slowly converted into the former by the action of hydrogen bromide

in glacial acetic acid, further action yielding 2-bromo-3 : 4 : 6-triphenylpyridine. On boiling (IV) with methyl-alcoholic potassium acetate solution, two stereoisomeric *2-cyano-1-benzoyl-2 : 3-diphenyl*cyclo*propanes*, prisms, m. p. 172° and 143°, respectively, were produced, a third isomeride, fine needles, m. p. 178°, b. p. 275°/29 mm., being obtained by prolonged action. The cyano group is completely inactive in all three isomerides. The isomeride of m. p. 172° was reduced to the nitrile (*b*) by the action of zinc dust in glacial acetic acid, the other isomerides yielding the nitrile (*a*). The action of methyl-alcoholic potassium hydroxide produced two stereoisomeric *β-cyano-γ-hydroxy-βγ-diphenylbutyrophenones*, stout needles, m. p. 156° (*c*) and 218° (*d*), respectively, the former being obtained from the isomeride of m. p. 172°, the latter from the others. The compound (*c*) was converted into (*d*) by solution in glacial acetic acid, the reverse change being effected by the action of methyl-alcoholic hydrogen chloride. Both isomerides yielded the hydrated *acetate*, $C_{25}H_{21}O_3N,H_2O$, stout needles, m. p. 121°, which yielded the anhydrous *acetate*, $C_{25}H_{21}O_3N$, microcrystalline plates, m. p. 142°, on boiling with acetyl chloride. On oxidation, *α-cyano-αβ-dibenzoyl-α-phenylethane*, prisms, m. p. 206°, was produced. β-Cyano-γ-hydroxy-βγ-diphenylbutyrophenone, m. p. 218°, was also synthesised by condensing benzaldehyde with the nitrile (I) in presence of potassium methoxide. The action of magnesium methoxide on methyl 3-cyano-2-benzoyl-1-phenyl*cyclo*propane-3-carboxylate (A., 1923, i, 54) afforded *methyl α-cyano-β-benzoyl-γ-phenyl-Δ$^{\beta}$-butenoate*, $CHPh{:}C(COPh)\cdot CH(CN)\cdot CO_2Me$, prisms, m. p. 104°. F. G. W.

Study of the Freezing of Solutions as a Method of Investigating some problems in Pure Chemistry. I. Systems containing *sec.*-Butyl Alcohol and its Derivatives. R. H. Lombaers (*Bull. Soc. chim. Belg.*, 1924, **33**, 232—245).—The system phthalic anhydride–*sec.*-butyl alcohol gives a normal freezing-point curve provided that the system is not subjected to prolonged heating at temperatures above 110°; under the latter conditions, the phthalate is formed in equilibrium with its components. This reaction is considered to be reversible, since the products of dissociation can be extracted from the fused phthalate. The equilibrium conditions between the phthalate and each of its components in excess were studied separately. With the anhydride, a normal curve indicating a eutectic at 53·6° (95 mols. anhydride, 5 mols. phthalate) was observed; with the alcohol, the eutectic could not be detected, and no evidence of the formation of a neutral phthalate was obtained. The freezing-point curves of mixtures of the racemic and active forms of the phthalate are of a type not hitherto observed. F. B.

Potassium Salts of Phenolphthalein. H. Bassett and D. J. T. Bagnall (*J. Chem. Soc.*, 1924, **125**, 1366—1373).—The system phenolphthalein–potassium hydroxide–water at 25° gives results rather less definite than those obtained with the sodium

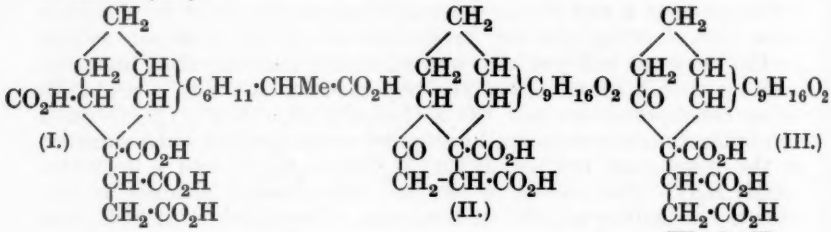
compounds (T., 1923, **123**, 1291), the curves corresponding with the hydrates of the mono-, di-, and tri-potassium salts being practically continuous. The mono-potassium salt gave hydrates with 5, 4, and 3 mols. of water; the di-salt with 10, 9, and 8 mols., and the tri-salt with 9, 8, 7, 6, 5, and 4 mols. of water. The tri-potassium salt as tetrahydrate can exist in contact with a range of solutions in which the ratio potash : phenolphthalein is less than that for the tri-salt and also with solutions supersaturated with respect to $KOH,2H_2O$ (cf. Pickering, T., 1893, **63**, 890). No red salt was obtained as a solid phase, but dehydration experiments indicated that a red salt of phenolphthalein can exist in the solid state. By heating the dry tripotassium salt to constant weight at 150° a deep red product was obtained corresponding in composition with a dihydrate of the tripotassium salt. It is probably either the dipotassium salt, $CO_2K{\cdot}C_6H_4{\cdot}C(C_6H_4{\cdot}OK){:}C_6H_4{:}O$ (formed by elimination of potassium hydroxide) or an equimolecular mixture of the mono-salt, $CO_2K{\cdot}C_6H_4C(C_6H_4{\cdot}OH){:}C_6H_4{:}O$, and a hydrate, $2KOH,H_2O$. The colour of the red dehydration product is unaltered on heating at 100° in a current of dry carbon dioxide, but in contact with the mother-liquors from the tripotassium salt the red colour disappears. The dry, colourless monopotassium salt partly melts in its water of crystallisation at 100°, giving a deep red, viscous mass, whilst on treatment with water it gives a red solution and a precipitate of phenolphthalein. R. B.

Bile Acids. XX. Conversion to a Tricarboxylic Acid. H. Wieland and O. Schlichting (*Z. physiol. Chem.*, 1924, **134**, 276—289; cf. A., 1921, i, 346; 1922, i, 41).—The second reaction product already described as resulting, together with norsolanellic acid, from the oxidation of pyrodeoxybilianic acid with fuming nitric acid proves to be a *tetracarboxylic acid*, $C_{16}H_{24}O_8$. It is prepared more conveniently by the action of fuming nitric and sulphuric acids on the diketo acid, $C_{23}H_{34}O_6$, obtained from pyrodeoxybilianic acid by oxidation with permanganate. It has m. p. 218° (decomp.). Its *methyl* ester, formed by the action of diazomethane, has b. p. 200—207°/0·3 mm. The acid on heating gives a monoketodicarboxylic *pyro acid*, $C_{15}H_{22}O_5$, m. p. 187°; this is oxidised by nitric acid to an optically active *tricarboxylic acid*, $C_{13}H_{20}O_6$, m. p. 187°, with slight sintering; on heating, it gives an *anhydride*, $C_{13}H_{18}O_5$, m. p. 147—148°. For the interpretation of these results in relation to the structure of the bile acid molecule, the original paper must be consulted.

C. R. H.

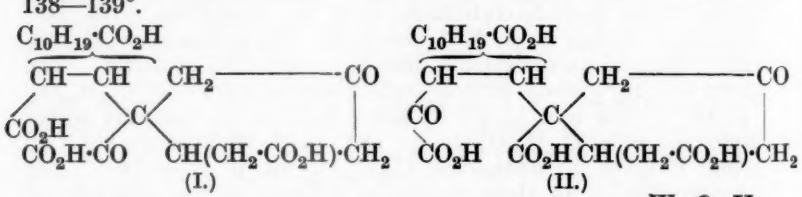
Bile Acids. XVIII. Chollepidanic Acid. H. Wieland [with B. Flaschenträger and A. Rewolle] (*Z. physiol. Chem.*, 1924, **134**, 140—148).—When deoxybilianic acid (20 g.) is heated for 2 hours with 100 c.c. of fuming nitric acid (*d* 1·52), there is formed, along with choloidanic acid and two other acids, chollepidanic acid, $C_{21}H_{30}O_{10}$ (cf. Wieland, A., 1921, i, 113). The yield of the purified acid is about 25% of the deoxybilianic acid used. It blackens and decomposes but does not melt at 280°. To this

acid formula (I) is assigned. The *pentamethyl* ester, $C_{21}H_{25}O_5(OMe)_5$, glistening needles arranged in rosettes, m. p. 102°, is formed from the silver salt and methyl iodide. The *monomethyl* ester, m. p. 275°, is formed when hydrogen chloride is passed into a boiling alcoholic solution of the acid. When chollepidanic acid is heated in a vacuum, the tribasic *pyrochollepidanic acid*, $C_{20}H_{28}O_7$, m. p. 266°, is obtained, and to it is assigned formula (II). This acid may be oxidised by potassium permanganate in alkaline solution to a tetrabasic *acid*, $C_{19}H_{28}O_9$, m. p. 234°, with the probable constitution (III).



W. O. K.

Bile Acids. XIX. Further Oxidation of Pyrodeoxybilianic Acid. H. Wieland and W. Mothes (*Z. physiol. Chem.*, 1924, **134**, 149—157).—When the diketotetracarboxylic acid, $C_{23}H_{34}O_6$, obtained from pyrodeoxybilianic acid by oxidation (A., 1921, i, 112) is further oxidised at 66° with potassium permanganate, *norcilianic acid*, $C_{23}H_{32}O_{10}$, a tetrabasic acid, m. p. 122° (decomp.), and iso*norcilianic* acid, isolated as the *sodium* salt, $C_{23}H_{31}O_{10}Na$, are obtained. To these acids are assigned formulæ (I) and (II), respectively. On further oxidation with chromic acid, both yield biloidanic acid. Norcilianic acid forms a *semicarbazide* of the *semicarbazone*, $C_{25}H_{38}O_{10}N_6$, and when methylated with diazomethane yields a *pentamethyl* ester, m. p. 138—139°.



W. O. K.

Mechanism of Phenylhydrazone Formation. S. Bodforss (*Z. physikal. Chem.*, 1924, **109**, 223—259).—The reactions between phenylhydrazine and ketones and aldehydes have been studied kinetically. The conductivity method proving unsuitable, the reaction was followed by titrating the phenylhydrazine with silver nitrate. It is found that the velocity of the reactions with *m*-nitrobenzaldehyde and other aromatic aldehydes is determined by the rate of decomposition of an intermediate compound. With aldehyde in excess, the reaction gives a unimolecular constant. With hydrazine in excess, the results are complex. The reaction with

acetophenone is bimolecular in presence of excess of ketone, and probably unimolecular with excess of phenylhydrazine. S. B.

Polymorphic Nitrobenzaldehydehydrazones. F. D. CHATTAWAY and A. J. WALKER (*J. Chem. Soc.*, 1924, **125**, 1207—1215). —*o*-Nitrobenzaldehyde-2-chloro-4-bromophenylhydrazone, *p*-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone, and *p*-nitrobenzaldehyde-4-chloro-2-bromophenylhydrazone exist in two well-defined forms, a yellow or orange, labile form, separating first, and a dark red, stable form into which the labile is transformed in contact with a solvent. *p*-Nitrobenzaldehyde-2-chloro-4-bromophenylhydrazone is trimorphic, the least stable, yellow, hair-like, non-pleochroic needles changing into orange, monoclinic needles and these into dark red, orthorhombic crystals, the transition temperature of the latter change being about 154°. The solubility curves of the labile and stable forms of these hydrazones in alcohol are practically parallel and the solubility ratios, labile : stable, are exceptionally large. The rates of transformation of the labile forms in contact with different solvents were determined approximately and crystallographic measurements of the stable forms were made. The stable forms of the three *p*-nitrobenzaldehyde-2 : 4-dihalogenophenylhydrazones crystallise in the orthorhombic system, and those of *o*-nitrobenzaldehyde-2-chloro-4-bromophenylhydrazone and *p*-nitrobenzaldehyde-2 : 4-dibromophenylhydrazone (of which only one form was observed) in the monoclinic system. R. B.

Compounds of Magnesium Alkyl Halides with Carbonyl Compounds and the Reducing Action of Grignard Reagents. II. K. HESS and W. WUSTROW (*Annalen*, 1924, **437**, 256—273; cf. A., 1921, i, 777).—The reducing action of magnesium alkyl halides previously observed in the case of benzaldehyde (cf. also Leroid, A., 1922, i, 215) has now been studied with the unsaturated aldehydes crotonaldehyde and cinnamaldehyde, and in both cases the unsaturated alcohol was obtained. Cinnamaldehyde and magnesium *iso*butyl halides form at low temperatures bright yellow, stable additive compounds of 1 mol. of aldehyde and 1 mol. of Grignard reagent, which on decomposition with water yield α-phenyl-ε-methyl-Δ^{α}-hexen-γ-ol. On warming, the additive compound decomposes, giving *iso*butylene and a colourless compound, which on decomposition with water yields cinnamaldehyde. These changes are represented by co-ordination formulæ of the type previously suggested. If the co-ordination number 4 is assumed for magnesium (cf. Meisenheimer and Casper, A., 1921, i, 654), the first yellow compound (I) must be represented by $CH\leqslant\begin{matrix}CHO\cdots\\CHPh\end{matrix}\!\!>\!Mg\!<\begin{matrix}Br\\C_4H_9\end{matrix}$ but the corresponding substituted hydrocinnamaldehyde,

$$CHPh(C_4H_9)\cdot CH_2\cdot CHO,$$

has not been obtained on decomposition with water. An isomeric compound, $CHPh{:}CH\cdot CH\!<\!\begin{matrix}OMgBr\\C_4H_9\end{matrix}$ (III), has been obtained by

the action of magnesium ethyl bromide on α-phenyl-ε-methyl-Δ^{α}-hexen-γ-ol; on warming, this yields no butylene, but reacts with water, forming the secondary alcohol, $CHPh{:}CH{\cdot}CH(C_4H_9){\cdot}OH$, or its anhydro product, α-phenyl-ε-methyl-$\Delta^{\alpha\gamma}$-hexadiene. The two isomerides are also distinguished by their behaviour with acetyl chloride, the first leading to cinnamaldehyde and the second to α-phenyl-ε-methyl-Δ^{α}-hexen-γ-yl acetate. The colourless compound, $CHPh{:}CH{\cdot}CH_2{\cdot}O{\cdot}MgBr$ (II), on treatment with acetyl chloride, yields cinnamyl acetate, but no cinnamaldehyde.

The action of magnesium ethyl bromide on crotonaldehyde yields only Δ^{β}-hexen-δ-ol (Rief, A., 1906, i, 394). Magnesium sec.-*n*-butyl bromide yields chiefly *ε-methyl-Δ^{β}-hepten-δ-ol*, a mobile oil, b. p. 69—70°/18 mm., α_4^{20} 0·8473, n_D^{20} 1·44113, besides a little crotyl alcohol (*α-naphthylurethane*, long needles, m. p. 89°) and a little dicrotyl ether. Better yields of crotyl alcohol were obtained with magnesium *iso*butyl bromide and using phenetole in place of ether, *iso*butylene being also formed. The following constants of crotyl alcohol are given: b. p. 118°/764 mm., d_4^{20} 0·8539, n_{α}^{20} 1·41898, n_D^{20} 1·42403, n_{β}^{20} 1·43156, n_{γ}^{20} 1·43705. Magnesium *cyclo*hexyl chloride gives only α-cyclo*hexylbuten-α-ol*, a colourless oil of aromatic odour, b. p. 98—100°/13 mm., $d_4^{14\cdot5}$ 0·9225, n_{α}^{20} 1·47623, n_D^{20} 1·47987, n_{β}^{20} 1·48635, n_{γ}^{20} 1·49245.

Magnesium ethyl bromide and cinnamaldehyde yield the bright yellow additive *compound*, $CHPh{:}CH{\cdot}CHO,MgBrEt$, which with water yields α-phenyl-Δ^{α}-penten-γ-ol (Klages, A., 1906, i, 661) for which constants are given, and on heating with methyl alcohol loses ethylene, giving a *compound*, C_9H_9OBrMg, from which only resinous products were obtained. The analogous *additive* compound, $CHPh{:}CH{\cdot}CHO,MgBrC_4H_9$, obtained from magnesium *iso*butyl bromide or chloride at −10°, contains 1 mol. of ether which is only partly lost on drying. With ammonium chloride solution in the cold, it yields *α-phenyl-ε-methyl-Δ^{α}-hexen-γ-ol*, thin needles, m. p. 37°, b. p. 160—162°/15 mm. (*benzoate*, m. p. 59—60°). On boiling with methyl alcohol, the additive compound loses butylene, yielding a compound, $CHPh{:}CH{\cdot}CH_2{\cdot}OMgBr$, from which only resinous products could be obtained. If, however, the decomposition takes place in boiling ether, the product obtained has the same composition, but yields cinnamyl alcohol (p-*nitrobenzoate*, m. p. 74—75°), on treatment with water, and on treatment with acetyl chloride *cinnamyl acetate*, b. p. 140—141°/18 mm., d_4^{12} 1·0567, n_{α}^{12} 1·5369, n_D^{12} 1·54415, n_{β}^{12} 1·55915, n_{γ}^{12} 1·57267, and α-phenyl-ε-methyl-$\Delta^{\alpha\gamma}$-hexadiene. The additive *compound*, $CHPh{:}CH{\cdot}CHO,MgClC_4H_9$, from magnesium *iso*butyl chloride and cinnamaldehyde on treatment with acetyl chloride, yields cinnamyl acetate and α-phenyl-ε-methyl-$\Delta^{\alpha\gamma}$-hexadiene, whilst the compound obtained from magnesium ethyl bromide and α-phenyl-ε-methyl-Δ^{α}-hexen-γ-ol yields only the corresponding acetate and α-phenyl-ε-methyl-$\Delta^{\alpha\gamma}$-hexadiene. R. B.

Simplification of the Gattermann Synthesis of Aromatic Aldehydes. II. R. Adams and E. Montgomery (*J. Amer. Chem. Soc.*, 1924, **46**, 1518—1521; cf. this vol., i, 51).—Aldehydo

derivatives of phenols and phenol ethers may be prepared in good yields by saturating a cooled mixture of the phenol or phenol ether (1 mol.), powdered zinc cyanide (2 mols.), and benzene, with hydrogen chloride, adding powdered anhydrous aluminium chloride, and then passing in a slow stream of hydrogen chloride at 40—45° for 3—4 hours. The imine hydrochloride is precipitated by addition of excess of 10% hydrochloric acid, and hydrolysed to the aldehyde by refluxing. F. G. W.

Mobility of Organically Combined Chlorine in the Friedel-Crafts Reaction. Influence of the Solvent. CHOPIN (*Bull. Soc. chim.*, 1924, [iv], **35**, 610—614).—The rates of reaction between acetyl chloride and benzene in the following solvents decrease in the order benzene, light petroleum, chlorobenzene, bromobenzene, carbon disulphide, nitrobenzene, the reaction being carried out at 4° under reduced pressure, and its progress followed by determination of the hydrogen chloride liberated. In nitrobenzene, the reaction is much slower if the aluminium chloride is dissolved prior to the addition of the other reactants. Chromium chloride in chlorobenzene gave practically no reaction, whilst with ferric chloride the above temperature is too low. Naphthalene reacts more slowly, toluene more rapidly, than benzene. In the reaction between acetyl chloride and naphthalene, the product in light petroleum solution is a mixture of about equal parts of α- and β-naphthyl methyl ketones. In nitrobenzene, the β- predominates; in bromobenzene, the α- predominates, and is formed exclusively in chlorobenzene and carbon disulphide. F. G. W.

The Beckmann Rearrangement. A. LACHMAN (*J. Amer. Chem. Soc.*, 1924, **46**, 1477—1483).—Benzophenoneoxime decomposes when heated at 185°, either alone or in presence of sodium or potassium chloride (cf. Hantzsch and Kraft, A., 1892, 338) with formation of benzophenone and benzophenoneimine in approximately equimolecular proportions, nitrogen, oxides of nitrogen, and water. The latter hydrolyses some of the benzophenoneimine, yielding ammonia in amount corresponding exactly with the excess of benzophenone found in the reaction product. No benzanilide is formed, and the reaction forms a convenient method of preparing benzophenoneimine. Lehmann's observations (*Z. angew. Chem.*, 1923, **36**, 360) on the decomposition of benzophenoneoxime in presence of hydrogen chloride were verified, but the formation of benzanilide by less than one equivalent of hydrogen chloride at slightly higher temperatures, and even in presence of water, was demonstrated. It is concluded that the Beckmann rearrangement is the direct conversion of the oxime salt into the acid amide and free acid, according to the equation $CPh_2{:}NOH,HCl=COPh{\cdot}NHPh+HCl$. Pure benzophenoneoxime, of which a convenient method of preparation is described, has m. p. 143°. F. G. W.

Preparation of Anthraquinone Derivatives. H. A. E. DRESCHER, J. THOMAS, and SCOTTISH DYES, LTD. (Brit. Pat. 214765).—Imidoanthraquinones are obtained by treating a halogen deriv-

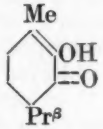
ative of anthraquinone with the imide of a dibasic acid (*e.g.*, phthalimide) or a metallic salt of the imide in the presence of metallic copper (*e.g.*, copper bronze) or a copper salt. The imidoanthraquinones are converted into aminoanthraquinones by hydrolysis, *e.g.*, with concentrated sulphuric acid. Substituted benzoylamidoanthraquinones are prepared by partial hydrolysis of phthalimidoanthraquinones, *e.g.*, with boiling, dilute sodium hydroxide.

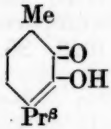
Details are given of the preparation of 1-*phthalimido*-, 2-*phthalimido*-, 1 : 5-*diphthalimido*-, 1-*chloro*-5-*phthalimido*-, 2-*nitro*-1-*phthalimido*-, 1-*amino*-4-*phthalimido*-2-*methyl*-, 1-*methylamino*-4-*phthalimido*-, and 2-amino-1-phthalimido-anthraquinones, and of their conversion into the corresponding aminoanthraquinones; also of the preparation of 2-benzoylamidoanthraquinone-2′-carboxylic acid by partial hydrolysis of 2-phthalimidoanthraquinone.

W. T. K. B.

Terpenes and Ethereal Oils. CXXVII. Diosphenol (Buchu-camphor) and Homologous Compounds. O. Wallach and A. Weissenborn (*Annalen*, 1924, **437**, 148—186; cf. A., 1916, i, 487; 1918, i, 440, 442).—Both dibromomenthone and dibromocarvomenthone yield, on treatment with alkali, the same product, diosphenol (buchu-camphor), and on treatment with ammonia in methyl-alcoholic solution give two isomeric monobrominated amines, which are stable in acid solution but in the presence of sodium hydroxide are both converted into diosphenol, with evolution of ammonia. If the ammonia is replaced by piperidine or other amines, stable, well-crystallised monobrominated bases can be isolated. In both cases, the tertiary bromine atom is the more mobile and the first step in the reaction is replacement of the bromine atom by an amine residue and not splitting off of hydrogen bromide. A mechanism is suggested to explain the conversion of both menthone and carvomenthone derivatives into diosphenol.

The structure of diosphenol has been established as 2-hydroxy-Δ^1-menthen-3-one (I), by its synthesis by oxidation of Δ^1-menthen-

(I.) 



(II.)

3-one through the 1 : 2-dihydroxyketone; carvenone (Δ^3-menthen-2-one) under similar conditions yields the isomeric form (II). The o-*cyclo*hexandiones do not appear to be capable of existence except under special conditions. The general name, diosphenols, is proposed for the homologous series of 1 : 2-hydroxy*cyclo*hexenones. They possess reducing properties, and give well crystallised dioximes derived from the *o*-diketones. These dioximes give complex compounds with the metals of the eighth group; the nickel compounds are characterised by their insolubility and intense

red or orange colour, and can be applied in the detection or determination of nickel. A dicyclic diosphenol obtained from β-ketodecahydronaphthalene by analogous methods possesses similar properties to the monocyclic diosphenols. On heating with potassium hydroxide the bicyclic diosphenol is converted into an α-hydroxy acid which on oxidation yields hydrindone, the six-membered ring being converted into a five-membered, as previously observed in the *cyclo*hexanone series (A., 1918, i, 442; 1919, i, 267).

The conversion of 2 : 4-dibromomenthone into diosphenol is most easily accomplished by treatment with ammonia in alcoholic solution, the brominated amine (syrupy hydrochloride) being more easily decomposed with sodium hydroxide than the *piperidide*, $C_{15}H_{26}ONBr$, needles or prisms, m. p. 127—128°, or *anilide*, $C_{16}H_{22}ONBr$, needles, (decomp.) 180°. Similarly, dibromocarvomenthone (1 : 3-dibromomenthan-2-one) yields a *bromopiperidide*, $C_{15}H_{26}ONBr$, m. p. 115—116°. Both the active and inactive preparations yield inactive diosphenol. With sodium methoxide, inactive 1 : 3-dibromomenthan-2-one is converted into *3-bromo-1-hydroxymenthan-2-one*, m. p. 92° (*acetyl* derivative, m. p. 155°), which is converted into diosphenol by treatment with alkali.

Oxidation of Δ^1-menthen-3-one with cold dilute potassium permanganate in acetone solution yields diosphenol, m. p. 83° (phenylurethane, m. p. 113—114°; cf. Asahina and Mituhori, A., 1922, i, 667). Carvenone under similar conditions gives an *oil* yielding the diosphenol reaction with ferric chloride. It dissolves in sodium hydroxide and, on acidifying, the diosphenol, m. p. 83°, separates. Both diosphenols yield the same dioxime, but the liquid diosphenol yields a *phenylurethane*, $C_{17}H_{21}O_3+H_2O$, m. p. 165—166°.

β-Ketodecahydronaphthalene (dibenzylidene derivative, m. p. 119—120°; α-ketotetrahydronaphthalene gives a *monobenzylidine* derivative, m. p. 206—207°) on bromination in acetic acid yields a viscous fluid which on shaking with 20% potassium hydroxide yields a dibasic *acid*, $C_{10}N_{16}O_4$, m. p. 165° (together with a lower melting acid, cf. Hückel, this vol., i, 31), and the *diosphenol*, $C_{10}H_{14}O_2$ (annexed formula), colourless, rhombic crystals, m. p. 88—89°. The *dioxime*, m. p. 196—197°, gives an intense bright orange precipitate with nickel salts. Besides the diosphenol, a small quantity of an isomeric *substance*, m. p. 99—100°, is formed, yielding a very insoluble deep red *dioxime*. On heating with potassium hydroxide at 120—130°, the diosphenol, m. p. 88—89°, yields a mixture of two acids difficult to separate. The more readily purified product is an *α-hydroxy acid*, $C_{10}H_{16}O_3$, m. p. 128—129°, which on oxidation with lead peroxide and sulphuric acid yields hexahydro-2-hydrindone, $C_9H_{14}O$ (semicarbazone, m. p. 240°; cf. Borsche and Lange, this vol., i, 33; *oxime*, m. p. 160—161°), a result which points to a ββ-structure for the diosphenol of m. p. 88—89°. The second *acid*, $C_{10}H_{16}O_3$, m. p. about 100°, on oxidation yields a mixture of ketones which give a semicarbazone with melting point

approximating to that of the semicarbazone of hexahydro-1-hydrindone.

The *monoxime* of buchu-camphor, m. p. 124° (cf. Kondakov, A., 1897, i, 227; Semmler, A., 1906, i, 373), gives a yellow solution in alkali, whereas the *dioxime*, m. p. 197°, gives a nearly colourless solution. The monoxime is stable in acid solution, but when the dioxime is boiled with dilute acid, diosphenol is partly regenerated. The dioxime gives a very insoluble orange *nickel* compound.

The simplest diosphenol, 2-*hydroxy*-Δ^1-*cyclohexen*-3-*one*, m. p. 38—40°, b. p. 193—195° (*phenylurethane*, m. p. 124°), was obtained from dibromo*cyclo*hexanone, m. p. 106—107°, by the action of potassium hydroxide. Concentrated potassium hydroxide converts it into 1-hydroxy*cyclo*pentane-1-carboxylic acid. With phenylhydrazine, it yields an osazone, golden-yellow needles, m. p. 152—153°, identical with that obtained from 1-hydroxy*cyclo*hexan-2-one; the *dioxime* has m. p. 189—190°, yields a *dibenzoyl* compound, m. p. about 170° (decomp.), and an intense red *nickel* compound, $C_{12}H_{18}O_4N_4Ni$, which can be used for the determination of nickel. On reduction with zinc dust and potassium hydroxide, the dioxime yields a colourless *base*, $(C_6H_9N)_2$, m. p. 108—109° (insoluble *picrate*), which is probably a phenazine of the structure

$$\begin{array}{l} CH_2\cdot CH_2\cdot CH\cdot N{:}C-CH_2\cdot CH_2 \\ \quad\quad\quad\

(*dioxime*, m. p. 163—164°, orange *nickel* compound). The diosphenol, $C_9H_{14}O_2$, m. p. 90°, prepared from dibromodihydro*iso*phorone (A., 1916, i, 487) is identical with the product obtained by oxidation of *iso*phorone (1 : 5 : 5-trimethyl-Δ^1-*cyclo*hexen-3-one) and must therefore be 2-hydroxy-1 : 5 : 5-trimethyl*cyclo*hexan-3-one (*dioxime*, m. p. 177—178°, orange-yellow *nickel* compound). R. B.

New Form of Fenchoneoxime. Characterisation of Fenchone in presence of Camphor. M. Delépine (*Compt. rend.*, 1924, **178**, 1721—1723).—When *d*-fenchone was treated with hydroxylamine in alkaline solution according to Rimini's method (A., 1896, i, 359), it gave, not the expected α-oxime (m. p. 165°, $[\alpha]_D$+47°), but a much more soluble compound, β-*fenchoneoxime*, m. p. 123°, $[\alpha]_D$+129·3°. This is converted into the usual α-form by being heated alone at 170—180°, or by evaporating its alcoholic solution to dryness, or by boiling an acidified alcoholic solution, or even if the solution is kept for some time. The reverse change, α into β, was not effected; although the formation of the β-variety evidently depended on the alkalinity of the mother-liquor, yet treatment of the α-form with alcoholic alkali hydroxide brought about no conversion. The two forms ($[\alpha]_D$—96°, and $[\alpha]_D$—47°, respectively) were also obtained from *l*-fenchone (cf. Wallach, A., 1893, i, 105).

A mixture of camphor and fenchone can be treated and so the proportion of fenchone determined. The oximes are separated by fractional crystallisation, taking advantage of the readier solubility of camphoroxime in alkaline media. W. A. S.

Reduction of Glycidic Esters in the Terpene Series. Synthesis of Inactive Citronellol and Rhodinol. A. Verley (*Bull. Soc. chim.*, 1924, [iv], **35**, 608—610).—Inactive citronellol and inactive rhodinol are obtained, respectively, by the reduction, with sodium and amyl alcohol, of the glycidic esters of α- and β-methylheptenones. Behal's failure to repeat the author's synthesis of nerol, and the action of ozone on methylheptenone are discussed. F. G. W.

Formation and Catalytic Decomposition of Terpinolene. A. Mailhe (*J. Usines Gaz*, 1923, **47**, 370—373).—Terpin, when passed over alumina in glass at 310—320°, yields terpinolene; terpineol yields a liquid, presumably terpinolene. The catalyst remains active for several days, and is easily regenerated by heat. Terpinolene passed over copper turnings at 500—550° gave a gas containing 27% C_nH_{2n}, 15% C_nH_{2n+2}, 18% CH_4, 40% H_2, and a liquid containing benzene, *cyclo*hexane, toluene, methyl*cyclo*hexane, *m*-xylene, and *m*-cymene. Chemical Abstracts.

Abnormal Phenomena in the Terpene Group in the Light of an Extension of Thiele's Hypothesis. K. Sławiński (*Roczniki Chemji*, 1923, **3**, 200—204).—Pinene and camphene behave abnormally on oxidation and addition of halogen acids

in that some derivatives are formed by the addition, for example, of the elements of water and oxygen to the double bond (formation of corresponding glycols) whilst others are due to the fission of the bridge (formation of bornyl chloride, sobrerol, etc.). It is suggested that these phenomena can be accounted for by assuming that the system formed by a ring conjugated with a double linking, such as is present in vinyltrimethylene, camphene, and pinene, behaves like a pair of conjugated double linkings towards oxidising and other agents (cf. Eisenlohr, *Spectrochemie der organischen Verbindungen*, 1912). G. A. R. K.

Essential Oil of *Pinus pinea*. G. Dupont and M. Barraud (*Bull. Soc. chim.*, 1924, [iv], **35**, 625—631).—The essential oil of *Pinus pinea* consists of *l*-limonene (75·4%) of greater optical activity ($[\alpha]_D$ −123·7°) than any natural limonene previously obtained, together with pinene (16·7%) and an inactive sesquiterpene, d^{15} 0·9157, n_D^{20} 1·4983 (6·6%). [Cf. *B.*, 1924, 615.] F. G. W.

New Synthetic Nitrophenol Glucosides and the Disinfectant Action and Toxicity of the Nitrophenols. E. Glaser and W. Wulwek.—(See i, 797.)

The Properties of Loroglossin and its Products of Hydrolysis, Dextrose and Loroglossigenin. M. Bridel and P. Delauney (*J. Pharm. Chim.*, 1924, [vii], **29**, 393—402; cf. A., 1919, i, 243).—Loroglossin, $C_{30}H_{42}O_{18}$, is an odourless and bitter glucoside which has been extracted from sixteen species of the order *Orchidaceæ* in the form of long, colourless needles, having no sharp m. p. (about 140—150°). The anhydrous substance gives $[\alpha]_D$ −45·65° in water, and −36·28° in 50% methyl-alcoholic solution. Its aqueous solution froths strongly when shaken. It gives a red colour with cold, concentrated sulphuric acid, but no coloration with cold nitric acid, hydrochloric acid, or ferric chloride. It is hydrolysed by sulphuric acid, giving 51·41% of dextrose and a substance, *loroglossigenin*, crystals, m. p. 77°, having an odour of mown hay. The substance is best obtained by the hydrolysis of loroglossin with emulsin, although the reaction proceeds slowly. It behaves like loroglossin towards sulphuric acid, but gives with ferric chloride a faint violet coloration, which disappears on shaking with ether or on warming. It has no reducing properties.
W. T. K. B.

Synthesis of Amygdalin. R. Campbell and W. N. Haworth (*J. Chem. Soc.*, 1924, **125**, 1337—1343; cf. Haworth and Wylam, T., 1923, **123**, 3120).—Ethyl *dl*-mandelate condenses with β-bromohepta-acetylgentiobiose in the presence of silver oxide, giving ethyl *dl*-hepta-acetylamygdalinate, m. p. 205°, $[\alpha]_D$ −62·0° (cf. Zemplén, this vol., i, 617). The same product was obtained by acetylation of *dl*-amygdalinic acid and crystallisation of the hepta-acetylamygdalinic acid from alcohol, when direct esterification takes

place, and by methylation of silver amygdalinate with methyl iodide followed by acetylation of the ester with acetic anhydride and sodium acetate, a by-product, m. p. 184—186°, $[\alpha]_D$ −28·6°, being obtained on one occasion. On treatment with ammonia in dry methyl alcohol, ethyl *dl*-hepta-acetylamygdalinate is converted into *dl*-amygdalinamide, a colourless, brittle solid, $[\alpha]_D$ −77·0°, which on acetylation in the presence of pyridine yielded *hepta-acetylamygdalinamide* in two isomeric forms, m. p. 166—167° and 152 153°, and $[\alpha]_D$ −68·6° and −49·7°, each containing 1 mol. of combined pyridine, which were separated by crystallisation from alcohol. The acetylated amide, m. p. 166—167°, on digestion with phosphoric oxide in xylene solution, yielded *d*-hepta-acetyl-amygdalin, $[\alpha]_D$ −36·2° (Caldwell and Courtauld, T., 1907, **91**, 671), the de-acetylation of which has already been effected by Fischer and Bergmann (A., 1917, i, 657). R. B.

Strophanthin. IV. Anhydrostrophanthidin and Dianhydrostrophanthidin. W. A. JACOBS and A. M. COLLINS (*J. Biol. Chem.*, 1924, **59**, 713—730; cf. A., 1923, i, 123; this vol., i, 65). —The action of 10% absolute alcoholic hydrochloric acid on strophanthidin at room temperature gives a product, $C_{25}H_{34}O_5$, which is characterised as the *ethylal* of *oxidoanhydrostrophanthidin*, needles, m. p. 223—230°; $[\alpha]_D$ −50°. On alkaline hydrolysis this gives an *acid*, $C_{25}H_{36}O_6$, rhombic plates, m. p. 120—125° (decomp.); *methyl* ester, m. p. 182—186°; $[\alpha]_D^{25}$ −81·7° in chloroform; on acid hydrolysis it gives anhydrostrophanthidin. If strophanthidin be boiled with 5% alcoholic hydrogen chloride 2 mols. of water are eliminated and the ethylal of oxidodianhydrostrophanthidin is formed, which, in turn, on acid hydrolysis gives dianhydrostrophanthidin, $C_{23}H_{28}O_4$. Both anhydro- and dianhydro-strophanthidin form an oxime, a phenylhydrazone, a monoacetate, and a monobenzoate. The substance, $C_{24}H_{30}O_4$, previously described by Windaus and Hermanns (A., 1915, i, 704) as anhydrostrophanthidin, has been identified as the methylal of oxidodianhydrostrophanthidin. A similar series of reactions has been carried through with dihydrostrophanthidin. The dianhydro derivatives both of strophanthidin and of dihydrostrophanthidin exhibit mutarotation.

It is concluded that the molecule of strophanthidin contains three hydroxyl groups, a carbonyl group and a lactone group. The formula of the basic hydrocarbon skeleton of strophanthidin becomes $C_{23}H_{40}$ and indicates the probable relationship of this substance to cholesterol and the bile acids.

Anhydrostrophanthidin, $C_{23}H_{30}O_5$, forms needles with $2H_2O$ from 50% alcohol; m. p. (air-dried) 223—226°, with slight sintering; $[\alpha]_5^{15}$ −145° in 95% alcohol; *oxime*, small prisms with $1H_2O$ from 95% alcohol; m. p. 260—265°; *phenylhydrazone*, needles containing $2H_2O$, m. p. (air-dry) 260—264°. The *acetate*, clusters of needles, sinters at 280° and melts at 292—294°. The *benzoate*, flat needles and platelets, sinters at 270° and melts at 287—289°.

The *ethylal* of *dianhydrostrophanthidin*, $C_{25}H_{32}O_4$, forms colourless

needles which on rapid heating sinter at 238° and melt at 249—251°; $[\alpha]_D^{22}$ −142° in chloroform. The *acid*, $C_{25}H_{34}O_5$, obtained by alkaline hydrolysis of the above, forms needles, m. p. 198—200° (decomp.), $[\alpha]_D^{26}$ −85·5° in chloroform; *methyl* ester, colourless needles, m. p. 152—156°. The *methylal* of *dianhydrostrophanthidin*, $C_{24}H_{30}O_4$, forms long needles sintering at 245°, m. p. 252—254°; $[\alpha]_D^{24}$ −131° in chloroform.

Dianhydrostrophanthidin, $C_{23}H_{28}O_4$, forms needles, m. p. 233—236°; $[\alpha]_D^{4}$ −222° in chloroform; *oxime*, stout prisms, m. p. 279—281° with effervescence, $[\alpha]_D^{25}$ −174° in pyridine; *phenylhydrazone*, needles or platelets containing $1·5H_2O$, m. p. (air-dry) 219—227°, $[\alpha]_D^{25}$ −245° in chloroform. The *acetate*, stout prisms with $0·5H_2O$, softens at 180° to a resin which melts at 203—206°, $[\alpha]_D^{22}$ −222° in chloroform. The *oxime* of the acetate forms platelets, m. p. 224—226°; the *oxime* of the *benzoate*, prisms, m. p. 283—285°.

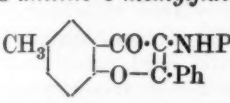
The *ethylal* of *oxidodianhydrodihydrostrophanthidin*, $C_{25}H_{34}O_4$, forms needles which sinter above 210°, m. p. 216—218°, $[\alpha]_D^{23}$ −101·3° in chloroform. *Dianhydrodihydrostrophanthidin* forms needles sintering at 190°, m. p. 193—199°, $[\alpha]_D^{4}$ −184° in chloroform. The *oxime* forms prisms, m. p. 291—292°. C. R. H.

Tannins and Similar Substances. XVI. Stereoisomeric Catechins. IV. K. FREUDENBERG and L. PURRMANN (*Annalen*, 1924, **437**, 274—285; cf. A., 1923, i, 697).—The previously studied relations of the stereoisomeric catechins and epicatechin have been further investigated with larger quantities of material, a good yield of *l*-epicatechin, together with a little *dl*-catechin, being obtained from the heartwood of *Acacia catechu*. The transformation of *d*-catechin and of *l*-epicatechin to *l*-catechin and *dl*-catechin is promoted considerably by the presence of a trace of potassium hydrogen carbonate. The epicatechins are rather less stable than the corresponding catechins, and *dl*-epicatechin is only obtained pure by mixing the *d*- and *l*-forms. The active forms are easily separated from the racemates and are recognised by their rotatory powers in alcohol, in the case of the epicatechins, and in aqueous acetone, disappearing in alcohol, in the case of the catechins. The data now available lead to the conclusion that the acacatechin examined by Perkin (T., 1905, **87**, 398) consisted largely of *dl*-catechin admixed with some *l*-epicatechin, a conclusion which has been confirmed by a series of mixed melting points of Perkin's derivatives with those of *dl*-catechin, and by the observation that *dl*-catechin always sinters 60—70° below its m. p. (205—210°) when epicatechin is present. The "catechin C" of Perkin and Yoshitake (T., 1902, **81**, 1167) obtained from Gambier catechin, m. p. 235—237° [disazobenzene derivative, m. p. 215—217° (decomp.)] appears to be identical with *d*-epicatechin, m. p. 245° (decomp.) [disazobenzene derivative, m. p. 216—218° (decomp.)], and the authors have isolated a small quantity of *d*-epicatechin from Gambier catechin. Bromotetramethyl-*d*-catechin has m. p. 172—173°, without decomposition (cf. Kostanecki and Krembs,

A., 1902, i, 637), and the acetate, m. p. 174—175°. dl-*Catechin tetramethyl ether* melts at 142°, the *monoacetate* at 134—135°, and the *toluenesulphonate* at 156—157°. dl-*Catechin pentabenzoate* melts at 181—182°, and the *pentamethyl ether* at 110—111°. d-*Epicatechin tetramethyl ether* melts at 93—94° and the *acetate* at 91—92°. The melting points and rotatory powers of the stereoisomeric catechins and epicatechins and their derivatives are tabulated.

R. B.

Anilino-flavones. K. von Auwers and O. Jordan (*J. pr. Chem.*, 1924, [ii], **107**, 330—357).—Auwers and Müller (A., 1909, i, 222) obtained by heating together in toluene solution aniline and 3-chloroacetyl-*p*-tolyl benzoate, *N*-benzoyl-3-phenylglycyl-*p*-cresol, and a by-product, m. p. 133—134°, now identified as 3-*anilino*-6-*methylflavone* (annexed formula). When the solvent used is benzene scarcely any of this product is formed, whilst if it be xylene, 22% of the theoretical yield is obtained. The authors discuss the mechanism of the reaction, and describe experiments on the stability of compounds of the type R·CO·CH_2·NH·Ph, the results of which bear on the question. 3-Anilino-6-methylflavone yields an unstable *hydrochloride* and *acetyl* (m. p. 165—167°) and *benzoyl* (m. p. 154—155°) derivatives, but no alkyl derivatives; neither can the latter be obtained by condensing 3-chloroacetyl-*p*-tolyl benzoate with, *e.g.*, methylaniline. With bromine in carbon disulphide it gives an unstable *compound*, m. p. 80—85°, and when the reaction mixture is heated, the p-*bromoanilinoflavone*, m. p. 154°, is formed, identical with the product of interaction of *p*-bromoaniline and 3-chloroacetyl-*p*-tolyl benzoate. When the flavone is heated with alcoholic sodium ethoxide, it breaks up, giving aniline, benzoic acid, *p*-hydroxytoluic acid, and benzanilide, together with unidentified products, whilst with the cold reagent partial conversion to *N*-benzoyl-3-phenylglycyl-*p*-cresol takes place.



Analogous flavone derivatives were prepared. The yields were poor, being mostly about 20% of the theoretical. *o*-Chloroacetyl-*m*-methoxyphenyl benzoate failed to react satisfactorily. 3-Chloroacetyl-*p*-tolyl benzoate and *o*-toluidine gives 3-*toluidino*-6-*methylflavone*, yellow needles, m. p. 107—108°; the corresponding compound with m-*toluidine* has m. p. 118—119°; with p-*toluidine*, m. p. 149·5°. 3-Chloroacetyl-*p*-tolyl *p*-methoxybenzoate yields with aniline 3-*anilino*-4′-*methoxy*-6-*methylflavone*, yellow needles, m. p. 151—152°, and the p-*anisidino*-analogue has m. p. 165—166°.

o-Chloroacetyl-*p*-methoxyphenyl benzoate forms colourless needles, m. p. 96—97°, and reacts with aniline to yield normally a *flavone*, m. p. 133—134°, and analogous products with o-*toluidine* (yield exceptional, viz., 45%, m. p. 162·5—163°), with m-*xylidine* (m. p. 95—96·5°), and with p-*anisidine* (m. p. 120—121°). o-*Chloroacetyl*-p-*methoxyphenyl anisate*, colourless needles, has m. p. 109·5—110·5°, but yields scarcely any flavone. 3-*Anilinoflavone*, the

simplest representative of the group, was obtained from o-*chloroacetophenyl benzoate* (colourless rods, m. p. 81—82°) and aniline. It forms yellow needles, m. p. 116°.

The following compounds are also described: m-*acetyl*-p-*ethoxytoluene*, m. p. 44—45°; *ethyl* o-*ethoxytoluate*, b. p. 143—143·5°/10 mm.; N-*methyl*-3-*phenylglycyl*-p-*cresol*, m. p. 87—88°; and its *benzoyl* derivative, m. p. 120—121°; 3-α-*bromopropionyl*-p-*tolyl anisate*, m. p. 86·5—87·5°; 3-α-*methylphenylglycyl*-p-*cresol*, m. p. 96·5—97·5°; 2-*chloroacetyl*-5-*methoxyphenyl anisate*, m. p. 152·5—153°; N-*acetyl*-3-*phenylglycyl*-p-*tolyl acetate*, m. p. 123—124°; and N-*acetyl*-3-*phenylglycyl*-p-*cresol*, m. p. 152—153°. W. A. S.

Preparation of Synthetic *d*- and *l*-ψ-Cocaine. E. Merck (Brit. Pat. 210050).—Racemic ψ-ecgonine methyl ester (cf. Willstätter and others, A., 1921, i, 122, and this vol., i, 70) is resolved and the optically active esters obtained are benzoylated with benzoic anhydride. Specimen resolutions by means of *d*-α-bromocamphor-β-sulphonic acid, *d*-α-bromocamphor-π-sulphonic acid, and malic acid are described. *d*-ψ-Ecgonine methyl ester *d*-α-bromocamphor-β-sulphonate forms crystals resembling a coffin-lid in shape and having m. p. 198° and $[\alpha]_D^{20}$ +71·5° (in 5% aqueous solution); it yields *d*-ψ-ecgonine methyl ester melting at 115° and identical with the natural product. Benzoylation of this ester with benzoic anhydride in benzene solution yields *d*-ψ-cocaine, m. p. 45°. The hydrochloride of the latter is sparingly soluble in water and has m. p. 205° and $[\alpha]_D^{20}$ +43° (in 5% solution). *l*-ψ-Ecgonine methyl ester *d*-α-bromocamphor-π-sulphonate has m. p. 243° and $[\alpha]_D^{20}$ +43·7° (in 5% aqueous solution). *l*-ψ-Ecgonine methyl ester has $[\alpha]_D^{20}$ −14·8° (in 10% methyl-alcoholic solution; it yields *l*-ψ-cocaine on benzoylation and the *r*-ester, m. p. 128°, when mixed with *d*-ψ-ecgonine methyl ester. *d*-ψ-Ecgonine methyl ester *d*-α-bromocamphor-π-sulphonate is a readily soluble salt, m. p. 130°. *l*-ψ-Ecgonine methyl ester *l*-malate is sparingly soluble and has m. p. 176° and $[\alpha]_D^{20}$ −18·2° (in 5% aqueous solution). The corresponding *d*-ester *l*-malate is soluble and melts at 142°.

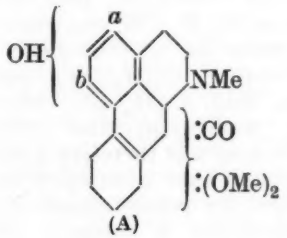
W. T. K. B.

Preparation of Tropacocaine from Javanese Coca Leaves. K. Hara and T. Sakamoto (*J. Pharm. Soc. Japan*, 1924, **503**, 33—38).—Tropacocaine is soluble in dilute ammonia; its hydrobromide is insoluble in water. Utilising this property, the authors have prepared tropacocaine hydrochloride from petroleum extracts of coca leaves produced in Java (yield about 1% of the crude extract). The residue, from which tropacocaine has thus been prepared, is then used as material for preparing cocaine. [Cf. *B.*, 1924, 653.] K. K.

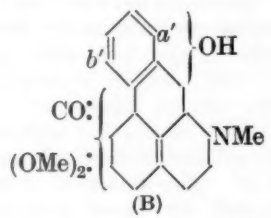
Alkaloids of *Datura alba*, Nees. S. Osada (*J. Pharm. Soc. Japan*, 1924, No. 504, 89—93).—The seeds of *Datura alba*, Nees, from the wild Formosa plant, on extraction with warm 96% alcohol, gave about 12% of brown oil, in which the following alkaloids were identified: *l*-scopolamine 0·24%, hyoscyamine 0·02%, and atropine

(as gold double salt) 0·0026%. A small amount of a *base* which gives a *chloroaurate*, m. p. 220°, was also obtained. K. K.

Alkaloids of Sinomenium and Cocculus. II. Constitution of Sinomenine. E. Ochiai (*J. Pharm. Soc. Japan*, 1924, No. 503, 8—23; cf. Kondo, Ochiai, and Nakajima, A., 1923, i, 1222; K. Goto, *J. Chem. Soc. Japan*, 1923, **44**, 795).—When treated in glacial acetic acid solution with bromine, sinomenine hydrochloride gives two *monobromides*; one, white needles, melts at 205° (decomp.), and the other, needles (obtained in larger amount), at 138° (decomp.). Both give a green coloration with ferric chloride. The iodine values (Wijs) of sinomenine and of its benzoyl derivative were found to be 143·9 and 53·89, respectively, whence sinomenine probably has the formula $C_{19}H_{23}O_4N$, and contains one ethylenic linking. When reduced by Skita's method, sinomenine affords *dihydrosinomenine*, $C_{19}H_{25}O_4N$, m. p. 199° (decomp.), $[\alpha]_D^{16}$ +170·5°. Sinomenine gives an *oxime*, m. p. 254°, and a *semicarbazone*, m. p. 264°, both of which give a green coloration with ferric chloride. Methyl- and dihydrosinomenine also give *semicarbazones*, the former of m. p. 252°, the latter of m. p. 207°. Thus, one oxygen atom in sinomenine is present in a carbonyl radical, the others in two methoxyl radicals and one phenolic hydroxyl radical. When sinomenine is heated with excess of benzoic anhydride in a sealed tube at 150—160° for 6 hours, a colourless, optically inactive *substance*, $C_{25}H_{22}O_5$ (m. p. 206°), is produced, which is insoluble in acids and alkalis and contains one ethylenic linking, probably produced by the breaking of a nucleus. When treated with ethyl chloroformate in alkaline solution, sinomenine gives a light non-crystallisable *substance*, $C_{25}H_{32}O_8NCl$, decomp. at 183°, $[\alpha]_D^{17}$ −108·4°. When distilled with excess of zinc dust, sinomenine affords considerable quantities of phenanthrene, and also of trimethylamine, and a small amount of an oily *substance* having an odour of quinoline. From these facts the author proposes one of the two following formulæ for sinomenine:



(A)



(B)

K. K.

Formation of Quaternary Ammonium Salts. II. E. de B. Barnett, J. W. Cook, and W. C. Peck (*J. Chem. Soc.*, 1924, **125**, 1035—1040).—The formation of quinolpyridinium salts, which had previously been shown to occur when *p*-benzoquinone was heated with the pyridine salts of inorganic acids, has now been

extended to salts of organic acids. Reaction takes place with difficulty, and the products can only be purified viâ the picrates. *Dihydroxyphenylpyridinium phenylacetate*, brown leaflets, m. p. 160°, was obtained by interaction of *p*-benzoquinone, pyridine, and phenylacetic acid.

The interaction of ethylenic compounds and pyridine–bromine mixtures has also been investigated. Well-defined *vic.*-bromopyridinium salts were obtained from anethole, *iso*safrole, *cyclo*hexane, and stilbene, the respective compounds formed being: β(or α)-*bromodihydroanethole*-α(or β)-*pyridinium bromide*, m. p. 170—172° (decomp.); β(or α)-*bromodihydrosafrole*-α(or β)-*pyridinium bromide*, m. p. 193° (decomp.); 1-*bromo*cyclo*hexane*-2-*pyridinium bromide*, m. p. 165—170°; β-*bromo*-αβ-*diphenylethylpyridinium bromide*, m. p. 190—193°, which after boiling with water and precipitated calcium carbonate gave β-*dihydroxy*-αβ-*diphenylethylpyridinium bromide*, m. p. 238—240°. Cinnamic acid yielded α-*bromo*-β-*phenylpropionic acid*-β-*pyridinium bromide*, m. p. 193—198° (decomp.), which on boiling with water or alcohol was converted into a *betaine*, m. p. 178—180°. *Methyl* α-*bromo*-β-*phenylpropionate*-β-*pyridinium bromide*, m. p. 178° (decomp.), and the corresponding *ethyl* ester, m. p. 157—158° (decomp.), were obtained from methyl and ethyl cinnamate respectively. Both of these esters when treated with ammonia gave methyl and ethyl α-bromocinnamates in 80—90% yield. The product obtained from safrole was too soluble to be isolated and probably consists of a dipyridinium salt. C. J. S.

Synthesis of Pyridine-ketones from Hydroxymethyleneacetone and -acetophenone. E. BENARY and H. PSILLE (*Ber.*, 1924, **57**, [B], 828—834).—An ethereal solution of ω-formylacetophenone was added to a saturated solution of ammonium acetate in glacial acetic acid and allowed to stand. Di-β-benzoylvinylamine, $(CHBz{:}CH)_2NH$, separated (Claisen's "ammonia compound of benzoylacetaldehyde," A., 1888, 690) which gave 1 : 3-diphenylpyrazole with phenylhydrazine (cf. Knorr, A., 1893, i, 230). From the acetic acid mother-liquor a base, $C_{18}H_{13}ON$, was recovered, colourless crystals, m. p. 89·5°; its *oxime* (m. p. 183—184°) with phosphorus pentachloride gave an *anilide*, $C_{18}H_{14}ON_2$, leaflets, m. p. 199°, which hydrolysed to an acid, $C_{12}H_9O_2N$, colourless needles, m. p. 220—229°, yielding 2-phenylpyridine (picrate, m. p. 175°) on heating with lime. The acid was therefore 2-*phenylpyridine*-5-*carboxylic acid*, and the original base 3-*benzoyl*-6-*phenylpyridine*. The latter is slowly attacked by permanganate and is unaffected by fused potassium hydroxide; it forms a yellow *picrate*, m. p. 175°; a colourless *hydrochloride*, m. p. 202°; a *nitrate*, m. p. 135—136°, and a *sulphate*, m. p. 137—138°. 3-Benzoyl-6-phenylpyridine with alcohol and zinc dust afforded 2-*phenyl*-5-α-*hydroxybenzylpyridine*, $OH{\cdot}CHPh{\cdot}C_5H_3NPh$, rhombohedra, m. p. 115—116° (*picrate*, m. p. 175—176°; *hydrochloride*, m. p. 173—174°). With phosphorus pentachloride the carbinol yielded 2-*phenyl*-5-α-*chlorobenzylpyridine*, m. p. 79°, reduced by acetic

acid and zinc dust to 2-*phenyl*-5-*benzylpyridine*, as leaflets, m. p. 63—63·5° (*picrate*, m. p. 145—146°; *hydrochloride*, m. p. 170°).

Treatment of sodium formyl-acetone with ammonium acetate and glacial acetic acid gave 3-acetyl-6-methylpyridine, b. p. 231—232° (cf. Knudson, A., 1895, i, 564), oxime, m. p. 182°. *Hydrochloride*, hygroscopic; *picrate*, m. p. 190°; *chloromercurate*, $C_8H_9ON{\cdot}HgCl_2$, m. p. 128°, and *methiodide*, m. p. 156·5°. On warming with nitric acid (1·42) 5-acetyl-2-methyl pyridine yielded 2-*methylpyridine*-5-*carboxylic acid nitrate*, m. p. 170—171°, which on distillation with lime yielded pyridine but no α-picoline; the nitrate yielded a dark green *copper* salt, $(C_5H_3NMe{\cdot}CO_2)_2Cu$, $(AcO)_2Cu$, from which the free acid was obtained, m. p. 207° (cf. Ladenberg, *Ann.*, 1888, **247**, 43). 3-Acetyl-6-methylpyridine, when condensed with formic ester by means of sodium ethoxide, gave the orange *sodium* salt of 5-*hydroxyacryl*-2-*methylpyridine*, $C_5H_3NMe{\cdot}CO{\cdot}CH{:}CH{\cdot}OH$ (*copper* salt, light olive-green). 5-*Hydroxyacryl*-2-*methylpyridine* was obtained as an unstable yellow oil by the action of sulphuric acid on the copper salt; it gave no precipitate with picric acid or with mercuric chloride. The sodium salt reacted with aniline to form 5-*hydroxyacryl*-2-*methylpyridine*-*anil*, $C_5H_3NMe{\cdot}CO{\cdot}CH{:}CH{\cdot}NHPh$, as pale yellow needles, m. p. 154—155°. F. A. M.

New Method in the *iso*Quinoline and its Ring Homologous Series. J. von Braun, G. Blessing, and R. S. Cahn (*Ber.*, 1924, **57**, [*B*], 908—912).—Ring closure with the formation of tetrahydro*iso*quinolines and *as*-homotetrahydro*iso*quinolines is readily effected by the successive action of phosphorus pentachloride and aluminium chloride on acylated derivatives of β-phenylethyl- and γ-phenylpropyl-glycine.

The *benzenesulphonyl* derivative of β-phenylethylglycine, $CH_2Ph{\cdot}CH_2{\cdot}N(SO_2Ph){\cdot}CH_2{\cdot}CO_2H$, m. p. 122°, is dissolved in nitrobenzene and treated successively with phosphorus pentachloride and aluminium chloride, thus giving 2-*benzenesulphonyltetrahydro*iso*quinoline*, m. p. 154° (yield 80%), from which tetrahydro*iso*quinoline is readily obtained, the over-all yield being about 50% of that theoretically possible. β-*m*-Tolylethylamine is converted by ethyl bromoacetate in ethereal solution into *ethyl* β-m-*tolylethylaminoacetate*, b. p. 165—167°/11 mm., which is transformed by concentrated hydrochloric acid into β-m-*tolylethylglycine hydrochloride*, m. p. 212—214°. The latter compound is converted into β-m-*tolylethylbenzenesulphonylglycine*, m. p. 105—106°, from which 2-*benzenesulphonyl*-6-*methyltetrahydro*iso*quinoline*, m. p. 102°, is derived. 6-*Methyltetrahydro*iso*quinoline* has b. p. 110°/11 mm., 255—256°/758 mm., d_4^{18} 1·0235; the *hydrochloride*, m. p. 195—197°, *picrate*, m. p. 205°, *nitroso* derivative, m. p. 98°, and quaternary *methiodide*, m. p. 144—145°, are described.

Ethyl γ-*phenylpropylaminoacetate*, b. p. 167—170°/11 mm., is transformed into γ-*phenylpropylglycine hydrochloride*, decomp. 201°. The non-crystalline *benzenesulphonyl* derivative of γ-phenylpropylglycine and the corresponding *toluene*-p-*sulphonyl* compound, m. p.

98—100°, are described. The latter substance is readily transformed in the usual manner into *toluene*-p-*sulphonyl*-as-*homotetrahydroisoquinoline*, m. p. 135°, from which the free base, $C_6H_4<^{[CH_2]_3}_{CH_2}>NH$, is obtained by hydrolysis. H. W.

Preparation of Compounds Related to the Acridines. British Dyestuffs Corporation, W. H. Perkin, and G. R. Clemo (Brit. Pat. 214756).—Dihydroacridines are obtained by reducing the corresponding acridones with sodium amalgam in hot alcoholic solution in presence of sodium hydrogen carbonate, carbon dioxide being passed through the reacting mixture. After removal of the alcohol, the dihydroacridine is precipitated by adding water. The dihydroacridines yield the corresponding acridines when oxidised (*e.g.*, with nitrous acid or chromic acid).

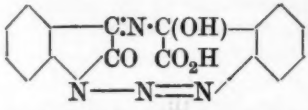
9-Aminodihydroacridine (almost colourless hairs, m. p. 114°), obtained by reducing 9-nitroacridone with sodium amalgam, is converted into 9-aminoacridine by acylating (to protect the amino group), oxidising as above, and hydrolysing the product.

W. T. K. B.

Products of the Action of Ammonia on Isatin. A. Reissert and H. Hoppmann (*Ber.*, 1924, **57**, [*B*], 972—981).—The constitution of many of the compounds isolated by Laurent in the years 1842 and 1845 has been elucidated.

Isatin ammonia [3-*amino*-3-*hydroxy*-2-*ketodihydroindole*], the primary product of the action of isatin and ammonia, is obtained when ammonia is passed into an ice-cold, alcoholic suspension of isatin until further separation of crystals does not occur; it readily loses ammonia when exposed to the air. If the stream of ammonia is interrupted as soon as the isatin is completely dissolved and the solution is then preserved, isatin-3-imide (Laurent's imesatin) is obtained in dark yellow, rectangular prisms, m. p. 175—176°, which is considerably more stable than the corresponding 2-compound. If the action of alcoholic ammonia on isatin is very protracted or if concentrated aqueous ammonia is used, 3-isatinimidyl-*o*-aminomandelic acid, $NH_2{\cdot}C_6H_4{\cdot}C(OH)(CO_2H){\cdot}N{:}C<^{CO}_{C_6H_4}>NH$ (Laurent's imasatic or isamic acid), is produced, which is more conveniently prepared by boiling isatin with ammonium acetate solution. It forms red, prismatic crystals, m. p. 164—165° (decomp.). The *ammonium* and *aniline* salt, m. p. 198°, and the o-*benzoyl* derivative, m. p. 188°, are described. The constitution of the acid is established by its synthesis from isatin-3-imine and ammonium isatate. The acid could not be converted into its cyclic anhydride, but when esterified, yields derivatives thereof of the type $NH<^{C_6H_4}_{CO}>C{:}N{\cdot}C(OH)<^{C_6H_4\cdots}_{C(OR)}>N$, of which the *methyl*, m. p. 186—187°, *ethyl*, m. p. 197°, and *propyl*, m. p. 181°, compounds are described; they are reconverted by sodium hydr-

oxide into the acid. Diazotisation of the latter substance in aqueous solution leads to the production of 3-*isatinimidyl*-o-N-*azomandelic acid* (annexed formula), m. p. about 140° (decomp.). If, however, ethyl nitrate is used, both hydroxy groups are esterified with formation of *ethyl* 3-*isatinimidyl*-o-N-*azophenylethoxyacetate*, m. p. 214—215°, which is hydrolysed to the corresponding *acid*, m. p. 195°. *Ethyl* 3-*isatinimido*-o-N-*azomandelate* has m. p. 214—215°.



When isatin is subjected to the prolonged action of aqueous ammonia, a phenolic substance (Laurent's imasatin), m. p. 230° after softening at 200°, is produced in addition to 3-isatinimidyl-*o*-aminomandelic acid. Since it can be synthesised by warming isatin and isatinimine in alcoholic solution, it is regarded as 3-isatinimidyl-3-dioxindole, although its genetic relationship to 3-isatinimidyl-*o*-aminomandelic acid could not be established. The *monobenzoyl* derivative decomposes above 240°.

Laurent's amasatin or isamide can be prepared by heating ammonium 3-isatinamidyl-*o*-aminomandelate, and is therefore 3-isatinimidyl-*o*-aminomandelamide; the corresponding *anilide* has m. p. 168°.

When isatin is treated with ammonia under pressure at the atmospheric temperature, Sommaruga's "di-iminoisatin or isatindiamine" is produced, which appears to be a polymeric isatinimine. At 100°, "hydroxydiaminodi-iminoisatin," $C_{16}H_{14}O_3N_6$, is also formed. H. W.

Preparation of a Monochloro Derivative of Antipyrine. A. LEULIER (*J. Pharm. Chim.*, 1924, [vii], **29**, 447—449).—A *monochloroantipyrine*, $C_{11}H_{11}ON_2Cl$, faintly yellow needles, m. p. 123—124°, is obtained by dissolving antipyrine in a 20% solution of chlorine and keeping the mixture for ¼ hour. The yield is smaller if sodium hypochlorite is used. Its aqueous solution gives a red coloration with ferric chloride. W. T. K. B.

Synthesis of Pyrazolealdehydes. II. C. A. ROJAHN and A. SEITZ (*Annalen*, 1924, **437**, 297—308; cf. this vol., i, 91).—The methods previously found successful in the preparation of pyrazole-4-aldehydes have been used in the synthesis of the 3(5)-aldehydes. The reduction of the acid chlorides affords, besides the aldehyde, oily by-products, which were found to be pyrazoles containing a methyl group less than was expected, carbon monoxide being lost in the reaction. It remains uncertain whether the decomposition is $R{\cdot}COCl \longrightarrow RH+CO+HCl$ or $R{\cdot}COH \longrightarrow RH+CO$. The 3- and 5-pyrazolealdehydes are for the most part oils with the general reactions of aromatic aldehydes. They do not undergo the benzoin or Cannizzaro reaction, the latter only affording traces of the carboxylic acid and resinous products (cf. Fischer and Zerweck, A., 1923, i, 364). 1-Phenyl-5-methylpyrazole-3-carboxylic acid with thionyl chloride yields 1-*phenyl*-5-*methyl*-

pyrazole-3-carboxyl chloride, m. p. 85° (*anilide*, m. p. 138°), which on reduction in xylene with palladium–barium sulphate catalyst, either with or without "sulphured" quinoline, gives 60—70% of the theoretical yield of 1-*phenyl*-5-*methylpyrazole*-3-*aldehyde*, d^{15}= 1·155 (*phenylhydrazone*, m. p. 173°; *semicarbazone*, m. p. 183°; *oxime*, m. p. 166°; *aminoguanidine nitrate derivative* (+1H_2O), $C_{12}H_{17}O_4N_7$, m. p. 155°). On shaking the bisulphite compound with aqueous potassium cyanide, the *hydroxynitrile* is formed, yellow needles, m. p. 121°. 1-Phenylpyrazole-5-carboxylic acid similarly yields 1-*phenylpyrazole*-5-*carboxyl chloride*, long needles, m. p. 53°, which on reduction with the catalyst and in the presence of a glowing copper spiral yields 1-*phenylpyrazole*-5-*aldehyde* (*semicarbazone*, m. p. 168°; *oxime*, m. p. 177°, *aminoguanidine nitrate derivative*, $C_{11}H_{12}N_6$,HNO_3, m. p. 192°), and a little 1-phenylpyrazole. By the condensation of ethyl acetylpyruvate with phenylhydrazine (cf. Claisen, A., 1894, i, 346) besides the 1-phenyl-5-methylpyrazole-3-carboxylic acid a higher melting product was obtained which with thionyl chloride yields 1-*phenyl*-3-*methylpyrazole*-5-*carboxyl chloride*, m. p. 39—41°, identified by conversion to the corresponding acid and amide. On reduction in the presence of a glowing copper spiral, 1-phenyl-3-methylpyrazole was obtained together with 1-*phenyl*-3-*methylpyrazole*-5-*aldehyde* (*aminoguanidine nitrate* derivative, m. p. 196°), which yields two *semicarbazones*, m. p. 166° and 195°, and two *oximes*, m. p. 146° and 179°, partial transformation of the lower-melting isomeride taking place in each case on seeding. 1-Phenyl-5-methylpyrazole-3-carboxylic acid on bromination in acetic acid solution yields 4-*bromo*-1-*phenyl*-5-*methylpyrazole*-3-*carboxylic acid*, white needles, m. p. 184°, converted to 4-*bromo*-1-*phenyl*-5-*methylpyrazole*-3-*carboxyl chloride*, long, lustrous needles, m. p. 78°, by thionyl chloride; the chloride on reduction yields 4-*bromo*-1-*phenyl*-5-*methylpyrazole*, b. p. 130° (*methiodide*, m. p. 206°), which was also obtained by brominating 1-phenyl-5-methylpyrazole, and 4-*bromo*-1-*phenyl*-5-*methylpyrazolealdehyde*, m. p. 71° (*oxime*, m. p. 194°; *semicarbazone*, m. p. 217°; *aminoguanidine nitrate* derivative, +1H_2O, m. p. 193°), the bisulphite liquor used in the separation yielding also some 4-*bromo*-1-*phenyl*-5-*methyl*-3-*hydroxymethylpyrazole*, m. p. 166—167° (*acetate*, m. p. 108°). 4-*Chloro*-1-*phenyl*-5-*methylpyrazole*-3-*carboxylic acid*, m. p. 221°, was obtained by the action of chlorine on a cold chloroform solution of 1-phenyl-5-methylpyrazole-3-carboxylic acid. R. B.

Conversion of Diketopiperazines into the corresponding Piperazines. E. Abderhalden, E. Klarmann, and E. Schwab (*Z. physiol. Chem.*, 1924, **135**, 180—187).—Piperazine hydrochloride was prepared from glycine anhydride by reduction with sodium, amyl alcohol, etc. *iso*Butylpiperazine dihydrochloride was similarly prepared from leucylglycine anhydride using sodium and ethyl alcohol. *Dibenzoylisobutylpiperazine* does not melt at 300°. The yields throughout were not good. The authors discuss the possibilities of the addition of amino-acids occurring through the imino

group or through the hydroxyl group of the tautomeric form of diketopiperazines. E. M. C.

Preparation of Compounds of Diketopiperazines with Amino-acids or Polypeptides. II. E. ABDERHALDEN and E. KLARMANN (*Z. physiol. Chem.*, 1924, **135**, 199—202).—Neither alanylglycine anhydride nor leucylglycine anhydride reacts with chloroacetyl chloride (cf. A., 1923, i, 1025). Glycine anhydride and α-bromo-γ-methylvaleryl chloride gave 1 : 4-*di*(*α-bromo-γ-methylvaleryl*)-2 : 5-*diketopiperazine*, m. p. 145°, which with ammonia gave glycine anhydride and leucinamide. E. M. C.

Synthetic Experiments in the Glyoxaline Group. A. SONN, E. HOTES, and H. SIEG (*Ber.*, 1924, **57**, [*B*], 953—959).—4-Chloro-1-methylglyoxaline is converted by formaldehyde at 130—140° into 4-chloro-1-methyl-2-hydroxymethylglyoxaline, m. p. 120° (cf. Sarasin, A., 1923, i, 711); the picrate, m. p. 150—151°, *hydrochloride*, m. p. 162°, additive *compound* with mercuric chloride, m. p. 161—162°, the *benzoate*, m. p. 75°, and its *picrate*, m. p. 167°, are described. The base is transformed by thionyl chloride into *4-chloro-1-methyl-2-chloromethylglyoxaline hydrochloride*, m. p. 167—168° (corresponding *picrate*, m. p. 156—157°), which is reduced by zinc dust and glacial acetic acid to *4-chloro*-1 : 2-*dimethylglyoxaline*, a yellow liquid (*picrate*, m. p. 175—176°), and by phosphorus and hydriodic acid to 1 : 2-dimethylglyoxaline. The catalytic reduction of 4-chloro-1-methyl-2-hydroxymethylglyoxaline yields 1-methyl-2-hydroxymethylglyoxaline, which is identified as the *picrate*, m. p. 136—137°. The following compounds are obtained from 4-chloro-1-methyl-2-chloromethylglyoxaline: *4-chloro-1-methyl-2-ethoxymethylglyoxaline*, a pale yellow, mobile liquid, and its *picrate*, m. p. 101—102°; *4-chloro-1-methyl-2-methylaminomethylglyoxaline picrate*, m. p. 178°; *4-chloro-1-methyl-2-dimethylaminomethylglyoxaline hydrochloride*, m. p. 198° (decomp.); *4-chloro-1-methyl-2-anilinomethylglyoxaline*, m. p. 125—126°, and its *picrate*, m. p. 170—171°; *4-chloro-2-p-ethoxyanilino-1-methylglyoxaline*, m. p. 114—115°. *4-Chloro-1-methyl-2-cyanomethylglyoxaline*, m. p. 128° after softening at 110° (*picrate*, m. p. 177—178°) is reduced by sodium and alcohol to *4-chloro-1-methyl-2-aminoethylglyoxaline*, which is analysed as the *picrate*, m. p. 176° after previous softening. The action of 4-chloro-1-methyl-2-chloromethylglyoxaline on the sodium derivative of ethyl α-cyano-β-ethylsuccinate and subsequent hydrolysis of the product with boiling concentrated hydrochloric acid leads to the isolation of *4-chloro-1-methyl-2-β-cyano-γ-carboxy-n-amylglyoxaline hydrochloride*, plates, decomp. 250° after darkening at 242° and (?) (γ)ethyl hydrogen β-cyano-α-4-chloro-1-methyl-2-glyoxalinylpentane-βγ-dicarboxylate,

$$\begin{matrix} CCl{-}N \\ \| \quad \gg C\cdot CH_2\cdot C(CN)(CO_2H)\cdot CHEt\cdot CO_2Et, \\ CH\cdot NMe \end{matrix}$$

m. p. 128° (*picrate*, m. p. 163—164° after slight previous softening). 4-Chloro-1-methyl-2-chloromethylglyoxaline gives a non-crystalline condensation product with ethyl sodiomalonate which is trans-

formed by successive bromination, hydrolysis, and elimination of carbon dioxide into a non-homogeneous, brominated monocarboxylic acid; the latter is converted by saturated aqueous ammonia at 50—60° into *ammonium α-amino-β-4-chloro-5-bromo-1-methylglyoxalinylpropionate*, m. p. 205—206° after previous softening (*picrate* of amino-acid, m. p. 231°).

Dimethyloxamide is converted by phosphorus pentabromide into *dibromo-1-methylglyoxaline*, colourless needles, m. p. 78—79° (picrate, m. p. 146°). H. W.

Stable and Labile Acyl Derivatives of the Indazoles. K. von Auwers and H. G. Allardt (*Annalen*, 1924, **438**, 1—33).—The 2-acyl derivatives of indazole and substituted indazoles have been examined, especially with regard to the stabilities of the labile forms (cf. A., 1919, i, 455; 1920, i, 638, 640; 1921, i, 806). The general method of the preparation of the labile forms is by the action of the silver salt of the indazole on the corresponding indazole in dry ether at 0° or by the interaction of the indazole and the acid chloride in dry pyridine or ether at 0°. The stable form is produced by the interaction of the sodium salt and the acid chloride under similar conditions. Many acyl indazoles are rather easily hydrolysed, especially the labile form; with hydrogen chloride in dry ether, the latter give indazole hydrochloride, whereas the stable form is unchanged after some hours. The effect of the acyl group on the stability of the labile acylindazoles has been examined. Preliminary experiments were carried out in sealed tubes, and the relative stabilities of some of the compounds are given as follows: *o*-nitrobenzoyl-, *o*-nitrocinnamoyl-, 2-nitro-5-bromobenzoyl- (stable after 1 year); *p*-nitrobenzoyl-, phenylacetyl-, carbonyl-; succinyl- (partly converted), *iso*butyryl- (converted in a few days), crotonyl- (1 day), *n*-butyryl- (somewhat more stable), propionyl- and acetyl- (unstable).

The following stable and labile 2-acyl derivatives have been examined, and the following values, amongst others, are given (*s*=stable; *l*=labile; rotatory dispersions are also given when refractive indices are given).

(*s*)-2-Acetylindazole, $d_4^{16\cdot8}$ 1·1886, $n_{He}^{16\cdot8}$ 1·58955; (*l*)-2-acetyl indazole, $d_4^{18\cdot7}$ 1·1007, $n_{He}^{18\cdot7}$ 1·62682; (*s*)-2-*chloroacetylindazole*, monoclinic prisms, m. p. 82—83°, b. p. 162°/10 mm., $d_4^{99\cdot6}$ 1·2636, $n_{He}^{99\cdot6}$ 1·57393; (*s*)-2-*dichloroacetylindazole*, stout white needles, m. p. 80—82°, b. p. 168—170°/13 mm.; (*s*)-2-*trichloroacetylindazole*, small prisms, m. p. 116—117°, hydrolysed by ethyl alcohol; (*s*)-2-*cyanoacetylindazole*, colourless crystals, m. p. 164—165°; (*s*)-2-*bromoacetylindazole*, fine needles, m. p. 73—74°; (*s*)-2-*α-bromopropionylindazole*, needles, m. p. 65—66°; (*s*)-2-n-*butyrylindazole*, colourless prisms, m. p. 61°, b. p. 150°/15 mm., $d_4^{33\cdot5}$ 1·1090, $n_{He}^{33\cdot5}$ 1·55854; (*l*)-2-n-*butyrylindazole*, small, glassy prisms, m. p. 86—87°, easily converted to stable form, $n_{He}^{12\cdot85}$ 1·62593 (in quinoline); (*s*)-2-iso*butyrylindazole*, oil, b. p. 132°/11 mm., $d_4^{12\cdot8}$ 1·1136, $n_{He}^{12\cdot8}$ 1·56534; (*l*)-2-iso*butyrylindazole*, oil, easily converted to α-form by ethereal hydrogen chloride, $d_4^{13\cdot0}$ 1·1159, $n_{He}^{13\cdot0}$ 1·57671; (*s*)-2-iso*valerylindazole*, b. p. 148—150°/11 mm., $d_4^{16\cdot3}$ 1·0879, $n_{He}^{16\cdot3}$

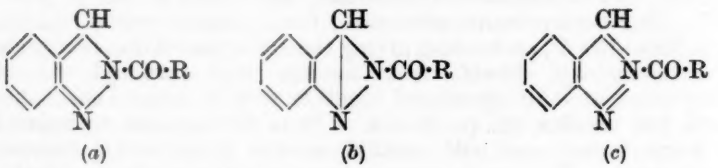
1·55466; (*l*)-2-iso*valerylindazole*, needles, m. p. 64° (approx.), unstable; (*s*)-2-*crotonylindazole* can only be prepared from the labile isomeride by standing over sulphuric acid, m. p. 78—80°; (*l*)-2-*crotonylindazole*, white, very hygroscopic crystals, m. p. 102°, resinifying on warming at 100°; (*s*)-2-Δ^{γ}-*pentenoylindazole*, b. p. 168—170°/16 mm., $d_4^{22\cdot6}$ 1·1172, $n_{He}^{22\cdot6}$ 1·57070; (*s*)-2-*nitrobenzoylindazole*, fine needles, m. p. 186—187°; (*l*)-2-*nitrobenzoylindazole*, fine, yellowish-green needles, m. p. 141—142°, stable, but by boiling in xylene, the (*s*)-isomeride produced, and by distillation under reduced pressure (13 mm.) this is also produced (b. p. 253—254°/13 mm.); (*s*)-2-m-*nitrobenzoylindazole*, stout, white crystals (benzene), needles (ether), m. p. 134°; (*l*)-2-m-*nitrobenzoylindazole*, very unstable; crystallisation from methyl alcohol hydrolyses the product; pale green, m. p. 142—144° (impure); (*s*)-2-p-*nitrobenzoylindazole*, fine needles, m. p. 164—165°; (*l*)-2-p-*nitrobenzoylindazole*, greenish-yellow, m. p. 137—138°, long heating giving the (*s*)-form; (*s*)-5-*bromo*-2-o-*nitrobenzoylindazole*, prisms, m. p. 186—187°; (*l*)-5-*bromo*-2-o-*nitrobenzoylindazole*, greenish-yellow needles, m. p. 189°, fairly stable, but slowly changed to the (*s*)-isomeride by heat; (*s*)-2-o-*chlorobenzoylindazole*, small prisms, m. p. 99°; (*l*)-2-o-*chlorobenzoylindazole*, fine, pale yellow needles, m. p. 76—77°, fairly stable; (*s*)-2-*phenylacetylindazole*, flat needles, m. p. 67—68°; (*l*)-2-*phenylacetylindazole*, m. p. 106—107°; (*s*)-2-o-*nitrophenylacetylindazole*, needles, m. p. 124—125°; (*l*)-2-o-*nitrophenylacetylindazole*, small needles, m. p. 107—108°, easily converted to the (*s*)-isomeride; (*s*)-2-*cinnamoylindazole*, fine needles, m. p. 120—121°; (*l*)-2-*cinnamoylindazole*, needles, m. p. 152—156°, not very stable; (*s*)-2-o-*nitrocinnamoylindazole*, fine needles, m. p. 185—187°; (*l*)-2-o-*nitrocinnamoylindazole*, fine, greenish-yellow needles, m. p. 156—157·5°, on heating giving the colourless stable isomeride; 2-*indazolecarboxyl chloride*, from indazole and carbonyl chloride in dry ether at −10° (produced together with di-indazyl carbonate) forms fine needles, m. p. 73—74°. It is decomposed to indazole by warm water, and with methyl alcohol gives *methyl indazole*-2-*carboxylate*. The *amide*, from ammonia and the above chloride, in ether forms needles, m. p. 167°. The labile form of the acid chloride could not be prepared. The following are also described: (*s*)-2 : 2′-*di-indazyl carbonate*, glassy needles, m. p. 137—138°, is prepared as a by-product of the above reaction and as main product on warming the acid chloride with indazole; (*l*)-2 : 2′-*di-indazyl carbonate*, from silver indazole and the above chloride in dry ether at −10°, is very unstable and has m. p. 149—151°; (*s*)-2-*indazolecarbanilide*, from indazole and phenylcarbimide or from the chloride and aniline, stout crystals, m. p. 104—105°; (*l*)-2-*indazolecarbanilide*, from indazole and phenylcarbimide in dry ether at −15°, crystals, m. p. 105—106°, is converted to the stable isomeride after heating for 2 hours; (*s*)-2 : 2′-*di-indazyl succinate*, small needles, m. p. 159°; (*l*)-2 : 2′-*di-indazyl succinate*, greenish-yellow needles, m. p. 140°, easily converted to the stable isomeride; 2-*indazyl hydrogen succinate*, needles, m. p. 146—147°, is prepared from silver indazole and succinyl chloride in dry ether and hydro-

lysing the *chloride* so obtained; (*s*)-2-*indazole*-p-*toluenesulphonate*, small, stout crystals; (*l*)-2-*indazole*-p-*toluenesulphonate*, small, six-sided crystals, easily changed to the (*s*)-isomeride; 2-*indazyl phenyl carbonate*, from 2-indazolecarboxyl chloride and sodium phenoxide in dry ether, m. p. 91°; 2-*indazyl* o-*nitrophenyl carbonate*, waxy needles, m. p. 97—98°, on distillation giving nitrophenylindazole (m. p. 153—154°, b. p. 245°/27 mm.); 2-*indazyl* p-*tolyl thiocarbonate*, long needles, m. p. 123°, decomposed on distillation under diminished pressure, giving a *compound*, m. p. 197—199°. 2-*Picrylindazole* from picryl chloride and indazole, golden, rhombic plates, m. p. 208—210°, possesses no basic properties. The refractive indices, rotatory dispersions, and densities are given of the following: (*s*)-2-*acetyl*-3-*ethylindazole*, $d_4^{51\cdot5}$ 1·0951, $n_{He}^{51\cdot5}$ 1·55639; (*s*)-2-*acetyl*-6-*methylindazole*, $d_4^{49\cdot95}$ 1·1623, n_{He}^{49} 1·58676; (*s*)-2-*propionyl*-5-*methylindazole*, d_4^{100} 1·0544, n_{He}^{100} 1·53682; (*l*)-2-*propionyl*-5-*methylindazole*, $d_4^{99\cdot4}$ 1·0505, $n_{He}^{99\cdot4}$ 1·55099.

The authors have shown that the presence of negative groups in aliphatic 2-acyl residues precludes the existence of the labile isomeride, but in aromatic acyl residues, with the negative group in the *o*- or *p*-position, the labile form has considerable stability, although if the negative group is in the *m*-position, the labile isomeride is less stable.

Attempts to prepare aminobenzoylindazoles by reduction of the corresponding nitro-compounds were unsuccessful. 2 : 2′-Diindazole derivatives of dibasic acids gave labile forms of varying stability.

Three possible formulæ are suggested for the acylindazoles:



(*a*) (*b*) (*c*)

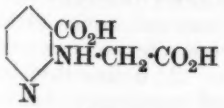
of which (*c*) is not considered seriously.

Spectrochemical experiments indicate (*a*) to be unlikely. The authors believe the isomerism to be steric in character and from measurements of the refractive index and rotatory dispersion it appears that formula (*b*) is the most likely for both isomerides. Against this, however, it is urged that the colour of certain of the labile isomerides suggests a quinonoid structure which would indicate (*a*) to be more likely; also that according to formula (*b*) the benzene ring and the 3-ring would not be co-planar, whereas for formula (*a*) the rings are co-planar; in the former case, isomerism would involve a large strain. Also if formula (*a*) be correct, hydrogen chloride should add on to the 1-nitrogen atom with difficulty in the case of one isomeride, owing to the proximity of the acyl group. This has been found to be true, the hydrogen chloride actually splitting off the acyl group. The question is left undecided. A. E. C.

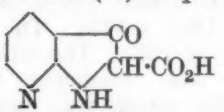
Carbonyldiphenylhydrazine. R. STOLLÉ (*Ber.*, 1924, **57**, [*B*], 1063—1066).—Carbonyldiphenylhydrazine was apparently obtained by Acree (A., 1903, i, 861) from αα-diphenylhydrazine-β-carbonyl chloride. Diphenylcarbamyl azide, m. p. 85° [decomp. $+x C_6H_6$, m. p. 61°; Toschi (A., 1914, i, 740), gives 78—79°] on heating in tetrahydronaphthalene or xylene gives the unsaturated radical, $Ph_2N{\cdot}CO{\cdot}N<$, but the carbonyl-diphenylhydrazine which is undoubtedly formed suffers rearrangement to 3-hydroxy-1-phenylbenzpyrazole, $C_6H_4<\begin{matrix}C(OH)\\NPh\end{matrix}>N$ (or the corresponding lactam) (cf. Curtius and Schmidt, A., 1923, i, 1080). This substance, dense crystals, m. p. 209°, is converted by methyl sulphate into a mixture of the *N*- and *O*-ethers, the latter forming colourless plates, m. p. 95° (cf. Konig and Reissert, A., 1899, i, 457). In moist tetrahydronaphthalene, diphenylcarbamylazide yields tetraphenylcarbazide, $(NPh_2{\cdot}NH)_2CO$. Ethyl ββ-diphenylhydrazinoformate, m. p. 141°, is obtained as a by-product when diphenylcarbamylazide is crystallised from alcohol. The action of carbonyl chloride on *o*-aminodiphenylamine yields *sym-di*-o : o′-*anilinodiphenylcarbamide*, m. p. 204°, and a small quantity of a *substance*, m. p. 160°, containing chlorine which with alkali or pyridine yields the above carbamide. The insensitiveness of diphenylcarbamylazide towards water, acids, and alkalis leads to the consideration of the phenylbenziminazolone formula, $C_6H_4<\begin{matrix}NH\\NPh\end{matrix}>CO$. The experiments to prepare carbonylhydrazines and benzpyrazolones are being continued. R. B.

Condensation of 2-Aminonicotinic Acid with Chloroacetic Acid to Derivatives of 1 : 7-Benzdiazole. E. SUCHARDA (*Roczniki Chemji*, 1923, **3**, 236—250).—So far no compounds analogous to indole or indigotin have been prepared containing pyridine in place of benzene rings. The synthesis of such compounds is now described.

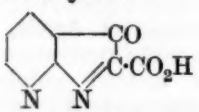
2-Aminonicotinic acid (Phillips, A., 1894, i, 301) condenses with chloroacetic acid in the presence of potassium carbonate to give a good yield of *pyridylglycinecarboxylic* acid (I) crystallising with $1H_2O$ and melting in the anhydrous condition at 218—219° (decomp.) with previous shrinking; the substance is strongly acid and forms a *sodium* salt, grey needles, $C_8H_7O_4N_2Na,3H_2O$. The action of mineral acids on the acid (I) leads to 3-*keto*-2 : 3-*dihydro*-1 : 7-*benzdiazole*-2-*carboxylic acid* (II) in quantitative yield.



(I.)



(II.)



(III.)

The new acid forms yellow crystals containing $1H_2O$ which is lost at 120°, the anhydrous substance melting at 220° (decomp.) with previous darkening; it is amphoteric in nature, the basic character predominating. The *hydrochloride* forms yellow needles, m. p. 284° (decomp.); the *sulphate*, $(C_8H_6O_3N_2)_2,H_2SO_4,4H_2O$,

forms yellow crystals, m. p. 225° (decomp.). By the action of sodium nitrate on the above sulphate the 1-*nitroso* derivative of the acid is produced; it is a microcrystalline, flesh-coloured substance decomposing violently at 250—260°, strongly acid in character, giving no compounds with mineral acids and dissolving in alkalis with a red colour. When heated with dilute sulphuric acid in a sealed tube the nitroso-compound gives 2-hydroxynicotinic acid, whilst the action of the concentrated reagent in an open vessel leads to 2-aminonicotinic acid. When the acid (II) is oxidised in ammoniacal solution with potassium ferricyanide or permanganate, the *dehydro* compound (III) is obtained, forming small, red needles, m. p. 259—260° (decomp.). The compound shows a fine violet-red colour in solution and dyes wool from an acid bath. It readily undergoes reduction. The dehydro-compound is also obtained by the action of atmospheric oxygen on solutions of the acid (II) in ammonia, but not in potassium or sodium hydroxides.

It is pointed out that the acid (I) differs from phenylglycine carboxylic acid by the greater stability of the carboxyl group in position 3 and the more ready formation of the indole derivative (II), whilst the latter shows characteristic behaviour on oxidation.

G. A. R. K.

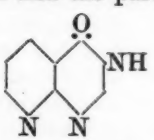
Hydroxylamine, Hydrazine, and their Derivatives as "Oxidising Agents" in the Formation of Induline. K. A. HOFMANN, F. HARTMANN, and F. KROLL (*Ber.*, 1924, **57**, [*B*], 945—963).—The formation of indulines of the benzene and naphthalene series from aniline and α-naphthylamine occurs, not only with typical oxidising agents, such as oxygen, but also with compounds of nitrogen which are generally placed among the strongest reducing agents, such as hydroxylamine, phenylhydroxylamine, hydrazobenzene, phenylhydrazine, and hydrazine. The latter substances are constrained by the energy conditions of ammonium salt formation to withdraw hydrogen from aniline and α-naphthylamine, thus leading to oxidation and production of indulines.

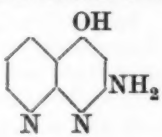
H. W.

Derivatives of Mono- and Di-substituted Hydrazodithiocarbonamides. E. FROMM and P. JOKL (*Monatsh.*, 1924, **44**, 298—305; cf. Fromm, Nerz, and Layer, A., 1923, i, 1239).—Monophenylhydrazodithiodicarboxylamide on boiling with 10% hydrazine hydrate solution and acidifying, yielded a mixture of 2-amino-5-thiol-1-phenyl-1 : 3 : 4-triazole, and 2 : 5-dithiol-1-phenyl-1 : 3 : 4-triazole (cf. Arndt, A., 1922, i, 375). The former substance yielded an *acetyl* derivative, m. p. 187°. The dithioltriazole was converted by methyl sulphate and ammonia into 2 : 5-dimethylthiol-1-phenyl-1 : 3 : 4-triazole, which was oxidised cautiously by permanganate to 2 : 5-*dimethylsulphonyl*-1-*phenyl*-1 : 3 : 4-*triazole*, m. p. 218°, the latter, when hydrolysed by alkali, giving 2-*hydroxy*-5-*methylsulphonyl*-1-*phenyl*-1 : 3 : 4-*triazole*, white prisms, m. p. 221°. 2 : 5-Dithiol-1-phenyltriazole gives with benzyl chloride and sodium ethoxide 2 : 5-*dibenzylthiol*-1-*phenyl*-1 : 3 : 4-*triazole*, m. p. 110°.

Diallylhydrazodithiodicarboxylamide when heated with hydrazine hydrate is converted into allylamine and 2 : 5-*dithiol*-1-*allyl*-1 : 3 : 4-*triazole*, m. p. 148° (*lead* derivative, $C_5H_5N\,S_2Pb$, decomp. 290°; *mercury* derivative, $C_5H_5N_3S_2Hg$, m. p. 188°, decomp. 280°). The allyltriazole is oxidised by bromine water to the *polysulphide*, $(C_5H_5N_3S_2)_n$, yellow crystals, m. p. 175°. Monoallylhydrazodithiodicarboxylamide when heated with 10% hydrazine hydrate solution yields 1-*amino*-2-*allylamino*-5-*thiol*-1 : 3 : 4-*triazole*, white prisms, m. p. 202° (*benzylidene* derivative, m. p. 204°). Monophenylhydrazodithiodicarboxylamide when oxidised by cold alkaline hydrogen peroxide affords 2-*amino*-5-*phenylamino*-1 : 3 : 4-*thiodiazole*, m. p. 205°, which forms a *benzylidene* derivative, yellow needles, m. p. 238°, a *benzoyl* derivative, m. p. 278°, and with acetic anhydride affords 2-*diacetamido*-5-*phenylamino*-1 : 3 : 4-*thiodiazole*, m. p. 264°. Monophenylhydrazodithiodicarboxylamide on treatment with hydrochloric acid in glacial acetic acid yields 2-*acetamido*-5-*thiol*-1 : 3 : 4-*thiodiazole*, m. p. 282°, which when treated with benzyl chloride and sodium ethoxide, gives 2-*acetamido*-5-*benzylthiol*-1 : 3 : 4-*thiodiazole*, m. p. 164°; the compound of m. p. 282° forms a *lead* derivative, $C_8H_8O_2N_6S_4Pb$, decomp. 250°, and with acetic anhydride yields 2-*diacetamido*-5-*thiol*-1 : 3 : 4-*thiodiazole*, m. p. 202°. F. A. M.

Derivatives of 1 : 3 : 8-Benztriazine and the Preparation of 2-Aminonicotinic Anhydride. L. Klisiecki and E. Suchardа (*Roczniki Chemji*, 1923, **3**, 251—260).—2-Aminonicotinic acid behaves in a manner analogous to that of anthranilic acid and condenses with formamide and acetamide, although the yield of condensation product is small. Thus on heating with formamide it yields 4-*hydroxy*-1 : 3 : 8-*benztriazine* (I), sparingly soluble, colourless prisms which do not melt at 385° (*hydrochloride*, colourless crystals). The 2-*methyl* derivative is obtained by substituting acetamide for formamide in the original condensation and forms colourless needles, m. p. 258°; the *hydrochloride* is somewhat sparingly soluble and was obtained in colourless needles. In contrast to the parent substance, the methyl derivative is readily soluble in water, etc., as well as in mineral acids and alkalis. This difference is accounted for by assuming the methyl derivative to have a lactim and the parent substance a lactam structure.

(I.) 

(II.) 

The alternative structure (II) is disproved because the substance does not show any of the characteristic reactions of the primary amino group. Moreover, the more acid nature of the above methyl derivative is shown by the fact that the chlorine in the hydrochloride cannot be estimated by direct titration as in the case of (I).

An attempt to condense methyl 2-aminonicotinate with ethyl acetate by means of sodium failed, the product forming colourless

prisms, m. p. 378° (decomp.); on acid or alkaline hydrolysis, it reverts to 2-aminonicotinic acid, of which it appears to be the *anhydride*, probably of the formula $C_{12}H_8O_2N_4$. G. A. R. K.

Amine Oxidation. IX. Hydrazyls. S. GOLDSCHMIDT (*Annalen*, 1924, **437**, 194—226; cf. A., 1920, i, 257; 1922, i, 475, 476).—A further series of investigations on different types of hydrazyls has revealed equilibrium conditions which do not conform to the Thiele-Werner principle, and the regularities observed by Wieland in the dissociation of tetra-arylhydrazines (A., 1911, i, 567; 1912, i, 904) do not hold for the substituted hydrazyls. The tetrazans of the α-acyl-α-β-diarylhydrazyls,

$$Ar(R\cdot CO)N\cdot N\cdot Ar \ldots$$

are much less dissociated than the hexa-aryltetrazans, and the following order is given: αα′-diacetyl-αβα′β′-tetraphenyltetrazan < α′α-dibenzoyl-αβα′β′-tetraphenyltetrazan < αα′-diacetyl-αβα′β′-tetratolyltetrazan < αα′-dibenzoyl-αβα′β′-tetratolyltetrazan. Dissociation of the tetrazan is thus weakened when the phenyl group is replaced by tolyl, and the αα′-diacetyl-αβα′β′-tetra(*m*-dimethylaminophenyl)tetrazan is almost completely dissociated into the hydrazyl. A further study of the effect of different acyl groups on the dissociation of diacyl-αα′ββ′-tetraphenyltetrazan, based on the reaction with αα-diphenyl-β-trinitrophenylhydrazine:

$$Ph_2N\cdot NH\cdot C_6H_2(NO_2)_3 + R\cdot CO\cdot NPh\cdot NPh \ldots \rightleftharpoons Ph_2N\cdot N\cdot C_6H_2(NO_2)_3 \ldots + R\cdot CO\cdot NPh\cdot NHPh,$$

showed that the dissociation did not depend on the dissociation constant of the acid, nor was a simple connexion observed between the solubility of the tetrazan and its degree of dissociation. The β-acyl-αα-diarylhydrazyls readily decomposed, and their behaviour was therefore studied in solution. Equilibrium between the hydrazyl and the tetrazan is a definite time reaction. The free hydrazyl reacts instantly with quinol: $2R_2N\cdot NR' \ldots + C_6H_4(OH)_2 \longrightarrow 2R_2N\cdot NHR' + C_6H_4O_2$, the solution being decolorised. The red colour, however, at once begins to reappear as the tetrazan dissociates, and the velocity of the dissociation increases greatly with the temperature, but decreases with dilution. The dissociation is also dependent on the nature of the solvent, and in the case of the tetrazan obtained from diphenylacetylhydrazine it was found that the dissociation and the solubility of the tetrazan are roughly proportional. With the dibenzoyltetrazans, the dissociation corresponds with Ostwald's dilution law. Confirmation of these results was obtained by a colorimetric method. Two formulæ are discussed for the acyl-αα-diarylhydrazyls, but in the absence of any satisfactory criteria for bivalent nitrogen and univalent oxygen, and in the absence also of evidence to the contrary, preference is given to the formula $R_2N\cdot\overset{|}{N}\cdot CO\cdot R$ previously used.

The behaviour of carbonic acid derivatives on oxidation has also been studied. Tetraphenylsemicarbazide and diphenyldimethylsemicarbazide yield deep blue solutions, which react at once (with decolorisation) with nitrogen dioxide, bromine, and triphenyl-

methyl. By the reaction with quinol these solutions are shown to contain the radicals $Ph_2N\cdot\overset{|}{N}\cdot CO\cdot NH\cdot NPh_2$ and

$$PhMe\cdot\overset{|}{N}\cdot CO\cdot NH\cdot NPhMe,$$

respectively. Both radicals are completely unimolecular in solution and at −70° obey Beer's law. They are distinguished by their reactivity towards hydrogen. The dimethyldehydro compound reacts quantitatively with quinol whilst only the tetraphenyldehydrocarbazide was isolated in the free state by the reaction with trinitrophenylhydrazyl. The dehydrogenation of the second nitrogen in the carbazide is probably possible although with difficulty, but the formation of hydrazyls from the corresponding urethane, $RR'N\cdot NH\cdot CO_2Et$, or chloride, $RR'N\cdot NH\cdot CO\cdot Cl$, was not observed. Triphenylsemicarbazide, $Ph_2N\cdot NH\cdot CO\cdot NHPh$, on oxidation with lead peroxide in benzene solution, leads exclusively to tetraphenyltetrazan,

$$2Ph_2N\cdot NH\cdot CO\cdot NHPh \longrightarrow 2Ph_2N\cdot\overset{|}{N}\cdot CO\cdot NHPh \longrightarrow Ph_2N\cdot\overset{|}{N}\cdot\overset{|}{N}\cdot NPh_2 + 2PhN{:}CO$$
$$\qquad\qquad\qquad

acetyl-αβ-diphenylhydrazine, m. p. 134°, and on oxidation, *αα'-dichloroacetyl-αβα'β'-tetraphenyltetrazan*, m. p. 102—104° (decomp.). *α-Propionyl-αβ-diphenylhydrazine*, tablets, m. p. 140·5°, on oxidation yields *αα'-propionyl-αβα'β'-tetraphenyltetrazan*, yellow rhomboids, m. p. 117° (decomp.).

[With R. WAGNER.]—αβ-Bis-*m*-dimethylaminophenylhydrazine with acetic anhydride is converted into α-acetyl-αβ-bis-*m*-dimethylaminophenylhydrazine, needles, m. p. 123°, which on oxidation with lead peroxide in chloroform solution at −20° yields a deep blue solution of the *hydrazyl*.

[With E. WOLFFHARDT.]—β-Acetyl-αα-diphenylhydrazine, obtained by acetylation of αα-diphenylhydrazine (Fischer, A., 1878, 190) on oxidation with lead peroxide in acetone solution, yields *ββ'-diacetyl-ααα'α'-tetraphenyltetrazan*, prismatic plates, m. p. 141° (decomp.), which on reduction with quinol yield the original hydrazine (m. p. 185°). With triphenylmethyl in chloroform solution the tetrazan yields triphenylmethyl peroxide and a *substance*, $C_{33}H_{28}ON_2$, dense crystals, melting at 159° to a red liquid, which on boiling with acetic acid yields triphenylcarbinol and acetyldiphenylhydrazine. In benzene solution a *substance*, $C_{33}H_{28}ON_2$, was obtained, darkening at 250°, m. p. 256°. β-Benzoyl-αα-diphenylhydrazine on oxidation with potassium ferricyanide in alcoholic solution yields the *β-benzoyl-αα-diphenylhydrazyl*, deep blue solutions, reconverted to hydrazine with quinol. *β-Anisoyl-αα-diphenylhydrazine* (from anisoyl chloride and diphenylhydrazine), m. p. 217°, on rapid treatment with sodium ethoxide in alcoholic solution is converted into the tetrazan, the original anisoyl hydrazine being very readily reprecipitated. *β-o-Nitrobenzoyl-αα-diphenylhydrazine*, citron-yellow needles, m. p. 203°, *β-m-nitrobenzoyl-αα-diphenylhydrazine*, yellowish-green needles, m. p. 205°, and *β-p-nitrobenzoyl-αα-diphenylhydrazine*, orange-yellow needles, m. p. 206°, are similarly prepared. The *o*-nitrobenzoylhydrazine on oxidation in toluene solution yields the *tetrazan*, bright yellow crystals rapidly changing to violet in the light.

[With A. WOLF.]—On oxidation with lead peroxide in a mixture of tetrachloroethane and toluene, tetraphenylcarbazide yields a deep blue solution stable at −25° but rapidly decomposing at the ordinary temperature. The *N-dehydrotetraphenylcarbazide* is isolated by the addition of αα-diphenyltrinitrophenylhydrazyl, the product, after washing from diphenyltrinitrophenylhydrazine with toluene, giving a dark violet solution in chloroform. Diphenyldimethylcarbazide on oxidation in chloroform–ether solution similarly yields a deep lavender-blue solution, from which the *N-dehydrodiphenyldimethylcarbazide* may be isolated as in the case of triphenylhydrazyl.

[With S. NATHAN.]—Triphenylchloromethane and αα-diphenylhydrazine in benzene solution yield *αα-diphenyl-β-triphenylmethylhydrazine*, m. p. 136—137° (turning brown at 126°), which on oxidation with lead peroxide in benzene solution yields tetraphenyltetrazene and triphenylcarbinol. Similarly, triphenylmethyl chloride and αβ-diphenylhydrazine in ethereal solution give *αβ-diphenyl-α-triphenylmethylhydrazine*, prismatic plates, m. p. 107°,

which is converted into triphenylcarbinol and azobenzene on oxidation with lead peroxide in alcoholic solution. *αα-Dibenzyl-β-tert.-butylhydrazine*, rhombic plates, m. p. 85°, from αα-dibenzylhydrazine and *tert.*-butyl bromide, yields only the unchanged hydrazine on oxidation. *αα-Dibenzyl-β-trinitrophenylhydrazine*, m. p. 176°, similarly prepared from picryl chloride, on oxidation yields trinitrophenylbenzylidenehydrazine, m. p. 262° (cf. Curtius and Dedichen, A., 1895, i, 29). α-Phenyl-β-trinitrophenyl-α-methylhydrazine on oxidation in chloroform solution at −70° yields a transient, dark violet solution, becoming yellowish-brown. At room temperature, oxidation yields a *substance*, $C_{26}H_{18}O_9N_{10}$, yellowish-red, rhombic crystals, m. p. 150°. R. B.

Halogenated Aromatic Hydrazines. I. 3 : 4-Dibromophenylhydrazine. E. Votoček and P. Jiřů (*Chem. Listy*, 1924, **18**, 113—117).—The 3 : 4-dibromophenylhydrazine prepared by Meyer (A., 1893, i, 155) by the bromination of acetone phenylhydrazone is shown to be the *p*-monobromo compound. The dibromo compound has now been prepared by reducing diazotised 3 : 4-dibromoaniline with stannous chloride; it forms fairly stable, yellow needles, m. p. 75°. It forms a *hydrochloride*, decomp. 215°, a *sulphate*, needles, decomp. 180°, an *oxalate*, decomp. 162—163°, and a *picrate*, decomp. 154—156°. The *acetyl* derivative forms red needles, m. p. 181—182°. The base forms *hydrazones* with the following compounds: benzaldehyde, yellow crystals, m. p. 128°; salicylaldehyde, reddish-yellow crystals, m. p. 190°; acetone, an oil; arabinose, a solid difficult to purify, decomp. 82—83°; rhamnose, m. p. 153—154°; dextrose, colourless crystals, m. p. 165—167°, and a colourless *compound*, m. p. 70°, containing less bromine; the compounds obtained from lævulose and galactose could not be obtained pure. The *osazone* prepared from dextrose or lævulose and the hydrochloride of the base forms yellow crystals, m. p. 225—226° (decomp.).

It is shown that both 3 : 4- and 2 : 4-dibromophenylhydrazine and also the *p*-bromophenylhydrazine obtained by Meyer give *p*-bromoaniline on reduction with zinc and hydrochloric acid.

G. A. R. K.

Preparation of *p*-Dialkylaminoarylphosphinous Acids. L. Cassella & Co., G.m.b.H. (Brit. Pat. 214836).—Phosphorus trichloride is heated with an excess of a dialkylarylamine and the resulting arylphosphorus chloride is converted into the *p*-dialkylaminoarylphosphinous acid or a salt of the same in the usual way (*e.g.*, with sodium hydroxide). The reaction is smooth and almost quantitative, and the products, which possess therapeutic properties, are of a high degree of purity. Details are given for the preparation of sodium 1-dimethylamino-4-phenylphosphinite, colourless needles ($+2H_2O$). Sodium 1-dimethylamino-4-phenyl-3-methylphosphinite forms scales, needles, or prisms ($+3H_2O$). Sodium 1-diethylamino-4-phenyl-3-methylphosphinite forms prisms ($+3H_2O$). Other salts of these acids are also described. W. T. K. B.

Compounds of the Diethylarsine Series. N. I. WIGREN (*Annalen*, 1924, **437**, 285—296).—Dehn's method (A., 1906, i, 150) failed for the diethylarsine series but *iododiethylarsine* (a yellow, irritating liquid, b. p. 70—71°/10 mm.) was prepared from diiodoethylarsine by Auger's method, as modified by McKenzie and Wood (T., 1920, **117**, 406). Oxidation of iododiethylarsine by hydrogen peroxide gives a diethylarsinic acid possessing properties sharply distinguished from those of the (probably impure) diethylarsinic acid described by Landolt (*J. pr. Chem.*, 1854, **63**, 283). It gives no precipitate with silver, ferric, lead, or copper salt solutions, whilst the acid barium salt described by Landolt could not be obtained. The behaviour of diethylarsine and bisdiethylarsineoxide (below) with mercuric chloride in hydrochloric acid shows that, contrary to the assumptions of Biginelli (A., 1901, i, 20) and Klason (A., 1915, i, 486), neither of these compounds can be the volatile arsenic compound produced by different arsenic moulds. The above iodo compound is converted by alkali into *bisdiethylarsineoxide*, $(AsEt_2)_2O$, a colourless, highly refracting liquid, b. p. 97—98°/10 mm., which has an unbearable, irritating odour, and oxidises to diethylarsinic acid in the air. Reduction of iododiethylarsine with zinc copper couple and alcohol (cf. Palmer, A., 1894, i, 400) in a specially designed apparatus affords *diethylarsine*, a colourless liquid, b. p. 105°, which undergoes spontaneous oxidation in air and has a garlic odour. With Biginelli's solution, it yields lustrous needles of the *mercurosochloride*, $AsEt_2Cl,2HgCl$, this, with boiling water, yielding chlorodiethylarsine. Diethylarsinic acid, colourless needles, m. p. 133—134° (Landolt gives 190°), forms a soluble *silver* salt (needles), and a *nitrate*, Et_2AsO_2H,HNO_3, prisms, m. p. 71—72°. The constants for the acid (by the methyl acetate, and Sörensen's indicator method [A., 1909, i, 861]) are $K_b=3{\cdot}7\times10^{-13}$. $K_a=3{\cdot}0\times10^{-7}$. R. B.

3-Amino-4 : 4′-dihydroxyarsenobenzene, and its *N*-Methylenesulphinate and *N*-Methylenesulphonate Derivatives. M. C. HART and W. B. PAYNE (*J. Amer. Pharm. Assoc.*, 1923, **12**, 688—695).—The preparation of 3-amino-4 : 4′-dihydroxyarsenobenzene and the determination of its toxicity are described, together with similar experiments with the (unstable) sodium *N*-methylenesulphinate and (more stable) sodium *N*-methylenesulphonate. The reduction with sodium hyposulphite of an equimolecular mixture of the two arsinic acids is not a general method for the production of unsymmetrical derivatives.

The loss of one of the essential anchoring groups from salvarsan does not impair its therapeutic efficiency.

CHEMICAL ABSTRACTS.

3-Amino-4-hydroxyarsenophenyl-4′-glycine and its *N*-Methylenesulphinate and *N*-Methylenesulphonate Derivatives. M. C. HART and W. B. PAYNE (*J. Amer. Pharm. Assoc.*, 1923, **12**, 759—768).—The toxic and maximum tolerated doses of 3-amino-4-hydroxyarsenophenyl-4′-glycine and its *N*-methylenesulphonate and *N*-methylenesulphinate have been determined;

the toxicity and trypanocidal activity decrease in the order given. The effect of the introduction of these groups (yielding soluble compounds) on the therapeutic activity is parallel to that in the case of salvarsan. Although these compounds are as effective therapeutically as the corresponding compounds of the salvarsan series, they are deficient in some of the essential anchoring groups considered by Ehrlich to be necessary for the highest type of therapeutic efficiency claimed to have been reached in salvarsan.

CHEMICAL ABSTRACTS.

Aromatic Selenonic Acids. II. *m*-Xyleneselenonic Acid. R. ANSCHÜTZ and F. TEUTENBERG (*Ber.*, 1924, **57**, [*B*], 1018—1023; cf. A., 1919, i, 24).—By the action of selenic acid on *m*-xylene in the presence of acetic anhydride a crystalline *m*-xylene-4(?)-selenonic acid, m. p. 130—130·5°, is obtained which presents analogies with *m*-xylene-4-sulphonic acid, but the position of the selenonic group has not been definitely determined. Fractional crystallisation gave no indication of the formation of the two possible isomerides. The yield, one of 75%, could not be improved, since concentration of the mother-liquor in a vacuum led to an explosion. *m*-Xylene-4-selenonic acid is stable towards boiling sodium hydroxide, is not attacked by hydrogen peroxide, and forms a *dihydrate*,

$$C_6H_3Me_2\cdot SeO_3H,2H_2O,$$

similar *dihydrates* of the *o*- and *p*-xylene-4-selenonic acids being described. The *o*-, *m*-, and *p*-xylene-4-sulphonic acids also yield dihydrates. The *salts* of 10 metals and *m*-xylene-4-selenonic acid are described, and the corresponding *m*-xylene-4-sulphonates, most of which are new (cf. Jacobsen, *Ber.*, 1878, **11**, 18), particular attention being directed to the number of molecules of water of crystallisation.

R. B.

Organo-chromium Compounds. V. Chromium Tolyl Compounds. F. HEIN and R. SPAETE (*Ber.*, 1924, **57**, [*B*], 899—908; cf. A., 1921, i, 826; 1922, i, 76, 77; this vol., i, 437).—The action of an ethereal solution of magnesium *p*-tolyl bromide on chromium chloride yields a mixture of chromium polyphenyl bromides from which the following substances are derived by methods which are somewhat modified from those used previously (*loc. cit.*): *chromiumpenta*-p-*tolyl carbonate*, $[Cr(C_7H_7)_5]_2CO_3,6H_2O$, orange crystals, m. p. 139—140°, and the corresponding tetrahydrate; the additive *compound* of chromiumpenta-*p*-tolyl bromide and mercuric chloride; *chromiumpenta*-p-*tolyl hydrogen anthranilate*, $2NH_2\cdot C_6H_4\cdot CO_2Cr(C_7H_7)_5,NH_2\cdot C_6H_4\cdot CO_2H$, m. p. 170° after previous softening; *chromiumtetra*-p-*tolyl hydrogen anthranilate*, $NH_2\cdot C_6H_4\cdot CO_2Cr(C_7H_7)_4,NH_2\cdot C_6H_4\cdot CO_2H$, m. p. 176° after previous softening; *chromiumtri*-p-*tolyl hydroxide*, *chromiumtri*-p-*tolyl iodide*, $2Cr(C_7H_7)_3I,Et_2O$, m. p. 115—119° (decomp.); *chromiumtri*-p-*tolyl hydrogen anthranilate*, an orange-yellow, amorphous substance, m. p. 145—149°; *chromiumtri*-p-*tolyl picrolonate*; *chromiumtri*-p-*tolylchromitetrathiocyanotodiammine*,

$$(C_7H_7)_3Cr\left[Cr\begin{matrix}(NH_3)_2\\(CNS)_4\end{matrix}\right],2H_2O,$$

an unstable, amorphous substance. The *p*-tolyl compounds are all considerably less stable than the corresponding phenyl derivatives, and this difference is even more noticeable with the *o*-tolyl compounds, of which *chromiumtetra*-o-*tolyl hydrogen anthranilate*, m. p. 75—110°, and *chromiumpenta*-o-*tolyl hydrogen anthranilate*, $C_{91}H_{89}O_6N_3Cr_2$, m. p. 151° (decomp.), are described. H. W.

Structure of the Protein Molecule. E. ABDERHALDEN and E. KOMM (*Z. physiol. Chem.*, 1924, **136**, 134—146).—When proteins are subjected to progressive partial hydrolysis with dilute hydrochloric acid or water alone at 150—160° for 7 hours, the greater part goes into solution. If the hydrolysate be then evaporated to dryness and the residue mixed with sand and extracted successively with ethyl acetate, chloroform, acetone, and methyl alcohol, it yields characteristic crystalline compounds having an anhydride structure, which can be readily isolated in the pure condition. They are optically inactive and do not give the ninhydrin reaction, indicating the absence of free amino and carboxyl groups. Regarding these compounds as fragments of the original protein molecule, it is concluded that in the protein molecule in addition to the polypeptide chains, anhydride-like residues having the diketopiperazine structure are also present. It is conceivable that these diketopiperazine residues are capable of existing in tautomeric forms, –NH·CO– ⟶ –N:C(OH)–, and the changes in the physico-chemical properties of proteins accompanying denaturation may be in part ascribed to this cause. When silk fibroin is hydrolysed with 0·5% hydrochloric acid as mentioned above, only a very small quantity of it is dissolved, but if the residue be then hydrolysed under the same conditions with four times its quantity of 2% hydrochloric acid it goes completely into solution. The first hydrolysate yields on extraction with ethyl acetate an *anhydride* containing (1 mol. of serine+1 mol. of glycine+3 mols. of alanine, *less* $5H_2O$). It forms needles, m. p. 213—215° (subl.). On treatment with alkali one-fourth of the total nitrogen appears as amino-nitrogen, and from this and other considerations the following structure is suggested:

$$N\lessdot\begin{matrix}CHMe\text{---}CO\\ C(OH)\cdot CH_2\end{matrix}\gtrdot N\cdot CO\cdot CH(NH_2)\cdot CH_2\cdot O\cdot C\lessdot\begin{matrix}N\cdot CHMe\\ CHMe\cdot N\end{matrix}\gtrdot C\cdot OH.$$

The residue from the above and the second hydrolysate on extraction with chloroform yield alanylglycine anhydride, m. p. 236°. The acetone and methyl alcohol extracts did not yield any characteristic products. Blood proteins on heating with water under pressure are completely dissolved and the hydrolysate on appropriate extraction yields leucine-imide, *iso*leucyl-leucine anhydride, and leucylglycine anhydride. D. R. N.

Reductive Decomposition of Proteins and Toxicity of their Decomposition Products. V. N. TROENSEGAARD (*Z. physiol. Chem.*, 1924, **134**, 100—112; cf. A., 1923, i, 615, 1243; this vol., i, 581).—Acetylated or methylated proteins (casein or gliadin) are reduced, hydrolysed, and fractionated as previously described. The basic fractions show marked toxic properties when injected into guinea-pigs. For the preparation of these hydrated protein deriv-

atives in addition to the methods previously described, acetylgliadin or acetylgelatin may be hydrogenated with magnesium in acetic acid solution and acetylcasein with zinc dust in acetic acid. W. O. K.

Oxidative and Reductive Scission of Proteins. S. EDLBACHER (*Z. physiol. Chem.*, 1924, **134**, 129—139).—Oxyprotosulphonic acid formed from casein by the action of potassium permanganate contains, as compared with casein, about 10% more humin nitrogen and about 10% less monoamino-nitrogen. After oxyprotosulphonic acid is hydrolysed by trypsin, the ratio of the number of methyl groups introduced by methyl sulphate to the formol titration number is the same as before hydrolysis. Further oxidation by hydrogen peroxide results in the formation of "*apo*casein," in which deep-seated changes, as shown by the distribution of nitrogen, have taken place. "*apo*Gelatin," "*apo*arachin," and "*apo*clupein" are also described.

[With K. ERBACH.]—The results of Troensegaard on the methylation, reduction, and subsequent hydrolysis of casein are confirmed (cf. preceding abstract). W. O. K.

Structure of the Protein Molecule. E. ABDERHALDEN and E. KOMM (*Z. physiol. Chem.*, 1924, **134**, 113—120; 121—128).—(I) From hog's bristles, hydrolysed in an autoclave with double their weight of 2% hydrochloric acid at 120° for 10 hours, the following compounds have been isolated, using the methods previously described (cf. this vol., i, 227): *Di(hydroxyprolyl)glycine anhydride*, $C_{12}H_{17}O_5N_3$, m. p. 174°, $[\alpha]_D^{22}$ −31·65° in alcohol; *isoleucyl-leucine anhydride*, m. p. 273—277°, $[\alpha]_D^{20}$ −15·96° in aqueous solution, and a product, m. p. 205—210°, possibly impure alanylglycine anhydride. From the proteins of blood, heated for 7 hours in an autoclave at 180° at 10 atm. pressure, the following products have been obtained: *leucylserine anhydride*, m. p. 201—204°, $[\alpha]_D^{20}$ +0·87° (in methyl-alcoholic solution), leucyl glycine anhydride, m. p. 233°, $[\alpha]_D^{20}$ −2·58° in alcoholic solution, and diprolylvaline anhydride, $[\alpha]_D^{20}$ +2·6°.

(II) In order to ascertain whether anhydrides such as are obtained from protein after partial hydrolysis may owe their existence to the conditions of hydrolysis, certain amino-acids and polypeptides have been heated with water for 7 hours at 150°. *l*-Leucylglycyl-*l*-leucine, *dl*-leucyldiglycylglycine, and glycyl-*dl*-leucylglycine, and probably glycyl-*dl*-leucine, yield leucylglycine anhydride. Diglycylcystine yielded no definite product and glycyl-*dl*-tyrosine only the component amino-acids. From the amino-acids, glycine, *d*-alanine, *dl*-leucine, and *l*-tyrosine, after heating with water under the same conditions by themselves or in mixtures, no trace of anhydride could be isolated. W. O. K.

Amide Nitrogen of Caseinogen. J. M. LUCK (*Biochem. J.*, 1924, **18**, 679—692).—Only two-thirds of the ammonia liberated by acid hydrolysis of caseinogen is obtained when this protein is submitted even to prolonged tryptic digestion. This undigested residue can be partly precipitated by alcohol and totally precipitated

by phosphotungstic acid and alcoholic mercuric chloride. The isolated residue entirely resists tryptic hydrolysis. When it is submitted to acid hydrolysis, glutamic acid and lysine are obtained. Eight to 10% of its total nitrogen occurs as ammonia, which is not associated with the lysine, but is present in amide form. It is concluded that glutamine or a glutamine-containing peptide is present in the tryptic digestion product of caseinogen. The possibility that this compound is a secondary product of enzymic synthesis cannot be excluded. S. S. Z.

Chemistry of Blood Pigments. F. HAUROWITZ (*Z. physiol. Chem.*, 1924, **136**, 147—159).—A method is described whereby oxyhæmoglobin can be prepared in the crystalline state in considerable quantity from horse-blood (cf. A., 1918, i, 316; 1921, i, 749; 1922, i, 962). The corpuscles are washed thrice by centrifuging with isotonic sodium chloride solution and then dialysed for 2 days against running ice-cold tap water and for 3 days subsequently against distilled water. The corpuscles are then hæmolysed and the dark red liquid is freed from the stroma by centrifuging, cooled with ice, and a current of air is passed through it, when within 10—20 minutes a dark red, crystalline magma begins to separate. The crystals are removed by centrifuging and further freed from moisture on unglazed porcelain tile and brought to 20% moisture content by pressing in a hydraulic press under a pressure of 300 atms. The above operations must be carried through as rapidly as possible as otherwise the product will not crystallise. The needles of oxyhæmoglobin are identical with those obtained by other methods (*loc. cit.*). Hæmoglobin can be readily prepared in a crystalline state without using alcohol by exposing a 40% oxyhæmoglobin paste in a vacuum until complete reduction is effected, when after one or two days it crystallises in hexagonal plates. Crystalline carbon monoxide–hæmoglobin can also be obtained by passing carbon monoxide through oxyhæmoglobin paste and keeping in a cool place. Nitric oxide–hæmoglobin can be prepared by passing nitric oxide free from the higher oxides of nitrogen through a 20% hæmoglobin solution, from which it rapidly crystallises on keeping in the cold. It decomposes on keeping into nitric oxide and hæmoglobin. The so-called water of crystallisation of oxyhæmoglobin preparations obtained by different methods is found to vary between 8·9 and 9·8%. D. R. N.

Biochemistry.

Pharmacology of Cell Respiration. IV. Influence of Temperature on the Spontaneous Oxidation of Hydrocyanic Acid in "Brennorten" ("Combustion Regions") and on the Curve of Oxygen Consumption of Tissues Poisoned by Potassium Cyanide. P. ELLINGER (*Z. physiol. Chem.*, 1924, **136**, 19—29).—In the presence of charcoal and a phosphate solution

of p_H 7·2, potassium cyanide absorbs oxygen at a rate which, for any given temperature, is proportional to the cyanide concentration. The rate of oxidation increases by 90—100% for a rise in temperature of 10°. A suspension of frog muscle pulp at p_H 7·2 shows an increase in rate of oxidation from 20—30° and a fall from 30—35° which becomes rapid between 35° and 40°, whilst in the presence of various cyanide concentrations frog-muscle shows a minimum rate of oxidation when the concentration of cyanide is 4·5 millimols. per litre at temperatures between 20° and 35°, and when the concentration is 2·25 millimols. at 40°. It is concluded that in addition to inhibiting cell oxidation, potassium cyanide is itself spontaneously oxidised in the tissues (cf. Meyerhof, *Pflüger's Archiv*, 1923, **200**, 1). J. P.

Respiration and Fermentation. H. F. Holden (*Biochem. J.*, 1924, **18**, 536—542).—The "respiration substance" of Meyerhof, obtained by extracting mammalian muscle with boiling water, is destroyed by aëration in contact with washed rabbit, rat, or frog muscle. The alcoholic co-enzyme in yeast or muscle is also destroyed in this way, although it is not readily oxidised by air alone. Neither glutathione nor pancreatic insulin can act as the alcoholic co-enzyme to washed "acetoned" yeast in the presence of potassium phosphate, at a suitable hydrogen-ion concentration at which the natural co-enzyme acts. The "respiration substance" seems to be a collection of irreversibly oxidisable substances, although not in the main lactic acid. A new method of preparation of "acetoned" yeast is described. S. S. Z.

Properties of an alleged Erythropoietic Hormone. C. D. Leake and F. J. Bacon (*J. Pharm. Exp. Ther.*, 1924, **23**, 353—363).—An erythropoietic substance was obtained by extracting with water a mixture of equal parts of desiccated preparations of spleen and red bone-marrow. The activity of the substance was not affected by boiling in aqueous solution or by keeping for long periods in sterile solution, but was destroyed by precipitation with alcohol and ether. The desiccated material, from which the hormone was obtained, contained about 0·24% of water-soluble iron and 2·89% of lecithin-phosphatides. C. R. H.

Spectroscopic Chemical Reactions of some Porphyrins and their Methyl Esters. O. Schumm (*Z. physiol. Chem.*, 1924, **136**, 243—278).—The occurrence of porphyrin (uroporphyrin), kotporphyrin (coproporphyrin), and chloroform-soluble porphyrin is reviewed and an account given of their spectroscopic reactions. Chloroform is not such a suitable solvent for the methyl esters of uroporphyrin and coproporphyrin as is phenol. In this case, the acidity is an important factor, and consequently, different results were shown with different samples of phenol. A phenol–alcohol mixture shows definite differences between the two esters, as does also a pyrrole–alcohol mixture. The latter, however, is unsatisfactory, owing to the brown coloration which develops in the

pyrrole itself. Less conclusive results were obtained with toluene, acetone, aniline, and benzene. Carbon tetrachloride, in which the esters are only very slightly soluble, gave definite differences.

The porphyrin prepared from normal fæces differs from both uroporphyrin and coproporphyrin, but is very similar to a preparation made from sulphur–hæmoglobin, and this, in turn, has spectroscopic properties very similar to those of ooporphyrin.

O. O.

Formation of Porphyrin from the Colouring Matter of Blood. O. SCHUMM and A. PAPENDIECK (*Z. physiol. Chem.*, 1924, **137**, 103—104; cf. this vol., i, 440, and preceding abstract).—In the preparation of a colouring matter allied to porphyrin, by the treatment of oxygen-free blood with hydrochloric acid, the authors have used chloroform to extract the substance from the reaction mixture. The substance thus obtained behaved in a somewhat anomalous manner, and it is now shown that this is probably due to partial esterification during the extraction with chloroform containing some alcohol. The solubility of the porphyrin derivative is greater in such chloroform than in pure chloroform. To avoid esterification, specially purified chloroform should be used. The preparation of the substance under discussion is greatly facilitated by the use of chloroform to which some alcohol has been added.

B. F.

Occurrence of Porphyrin in Blood-serum. A. PAPENDIECK (*Z. physiol. Chem.*, 1924, **136**, 293—306).—Contrary to the findings of Fischer and Zerweck (this vol., i, 459), and following their procedure, the author could find no positive spectroscopic evidence of the presence of porphyrin in a large number of samples taken from subjects in various conditions.

O. O.

Porphyrins from Blood-pigment. A. PAPENDIECK (*Z. physiol. Chem.*, 1924, **134**, 158—159).—Treatment of blood, saturated with hydrogen sulphide by fuming hydrochloric acid, yields a porphyrin, isolated by neutralising the solution with sodium carbonate, and acidifying with acetic acid, which precipitates the porphyrin. Treatment of the porphyrin with 1% methyl-alcoholic hydrochloric acid results in the formation of a *methyl* ester, insoluble in alkali, dense, prismatic rods, from methyl alcohol, m. p. 221°.

W. O. K.

Natural Porphyrins. VI. Distribution of Porphyrins in Organs. Detection of a Porphyrin in Yeast. H. FISCHER and K. SCHNELLER (*Z. physiol. Chem.*, **1924, 135**, 253—293).—Coproporphyrin accompanies Kämmerer's porphyrin in the products resulting from the putrefaction of calf liver, heart, and flesh, of ox flesh, and of human liver, spleen, lung, heart, and uterus. In human back-muscle, after removal of blood, coproporphyrin is alone demonstrable. Kämmerer's porphyrin is detectable in blood-corpuscles washed with physiological salt solution and subjected to putrefaction, whilst coproporphyrin may also be present in

traces if the serum has not been completely removed. Only one porphyrin is therefore derivable from red blood-corpuscles. The breast-muscle of the pigeon yields after putrefaction coproporphyrin, of which the origin is ascribed to degradation of the muscle pigment (myohæmoglobin) by lactic acid. Hydrolysis of fresh blood-corpuscles by hydrochloric acid, by pepsin, and by trypsin did not lead to the definite identification of the porphyrin. Coproporphyrin is present in putrefying fish flesh and in yeast, both fresh and putrefying. This evidence is regarded as lending support to the view that blood pigments are derived from leaf pigments with porphyrins occurring as intermediates. A possible parallelism between the dualism shown by the porphyrins and chlorophylls A and B is suggested. Kämmerer's porphyrin left in glacial acetic acid and ether for some months shows a band (623 $\mu\mu$) characteristic of hæmatoporphyrin. Coproporphyrin has been isolated as the crystalline methyl ester from fæces derived from a purely vegetarian diet (cf. A., 1923, i, 1244; this vol., i, 459).

J. P.

Changes of Reaction of Sera. H. Plotz and M. Schoen (*Compt. rend.*, 1924, **178**, 1926—1928).—Exposure of normal horse-serum in open tubes caused an increase in p_H value, owing to the escape of carbon dioxide. A decrease in p_H took place when serum was stored aseptically in closed tubes; in one case the p_H changed from 7·33 to 6·89 after storage for 51 days at 37°.

E. M. C.

Glycolysis in Blood of Normal Subjects and of Diabetic Patients. E. Tolstoi (*J. Biol. Chem.*, 1924, **60**, 69—75).—The blood of eight normal subjects and of eleven diabetic patients was examined. Determinations of sugar at intervals up to 24 hours in the blood kept at 37° with aseptic precautions showed no difference in the glycolytic power of diabetic and normal blood. At room temperature, the glycolytic rates were diminished to about the same extent in both types of blood. Counts of the red and white corpuscles gave figures within normal limits and bearing no relationship to the rate of glycolysis.

C. T. G.

Relation of p_H to Tungstic Acid Precipitation of Protein. A. T. Merrill (*J. Biol. Chem.*, 1924, **60**, 257—259).—In serum, the maximum precipitation of nitrogenous substances occurs on the acid side of p_H 5; in peptone solutions the zone of maximum precipitation is not reached until the acidity is greater than p_H 1.

C. R. H.

Neutral and Oxidised Sulphur in the Blood. J. Browinski (*Bull. Soc. Chim. biol.*, 1924, **6**, 352—356).—The deproteinised blood of horses and cattle was found to contain 9·5 to 12·0 mg. % of sulphur as sulphates and also a considerable quantity of unoxidised (neutral) sulphur. Ethereal sulphates were not found. Sulphates were precipitated and weighed as barium sulphate in the blood or serum previously deproteinised by means of trichloroacetic

acid. Allowance was made for the amount of barium trichloroacetate precipitated. Neutral sulphur was determined by subtracting the sulphur as sulphates from the total sulphur found by fusion with sodium peroxide and subsequent precipitation with barium. The results do not agree with those of Denis (A., 1922, ii, 225), who found much less sulphur as sulphates and no neutral sulphur in blood. The analytical methods employed by Denis are criticised. C. T. G.

Effect of Inorganic Salts on the Chemical Changes in the Blood of the Dog after Obstruction of the Duodenum. R. L. Haden and T. G. Orr (*J. Exp. Med.*, 1924, **39**, 321—330; cf. *ibid.*, 1923, **37**, 365, 377; **38**, 55).—Life is prolonged by sodium chloride; ammonium chloride produces an acidosis. Potassium, calcium, and magnesium chlorides do not prevent the usual rise of non-protein nitrogen and fall in chlorides, followed by death. The toxic process is hastened by iodides; the inhibitory effect of sodium bromide is much less than that of the chloride.

Chemical Abstracts.

Blood Changes and Clinical Symptoms following Oral Administration of Phosphates. H. A. Salvesen, A. B. Hastings, and J. F. McIntosh (*J. Biol. Chem.*, 1924, **60**, 311—326).—Oral administration to dogs of small doses of phosphates over a long period produced no clinical symptoms; if alkaline phosphates were used no change in the composition of the blood was observed, whereas with acid phosphates there was an increase in the phosphate concentration of the serum. The rapid administration of large doses of phosphate, acid or alkaline, produced violent symptoms of tetany, accompanied by a rise in the phosphate and a fall in the calcium of the serum. The tetany resembled that previously observed in parathyroidectomised dogs (cf. A., 1923, i, 979) and, in this case also, could be relieved by injection of calcium chloride. It is therefore probably due to a decrease in the calcium concentration of the blood. C. R. H.

Effect of Administration of Calcium Salts on the Inorganic Composition of the Blood. H. A. Salvesen, A. B. Hastings, and J. F. McIntosh (*J. Biol. Chem.*, 1924, **60**, 327—339).—Ingestion of calcium chloride produces an acidosis owing to the replacement of hydrogen carbonate ions by chloride ions in the blood. The intravenous injection of small quantities of calcium chloride produced no change in the acid–base equilibrium of the blood, but a rise in the phosphate concentration was observed. Although the calcium disappeared rapidly from the blood, it could not be subsequently recovered from the urine or fæces. In cases of Bright's disease, it was not found possible to restore the calcium content of the blood to normal by means of oral administration of calcium lactate. C. H. R.

Calcium Content of the Blood during Pregnancy. II. S. T. Widdows (*Biochem. J.*, 1924, **18**, 555—561).—The results

for abnormal pregnancies support the observation for normal pregnancies; a heavy demand of the fœtus for calcium at certain stages of its development is met by a perfectly balanced calcium metabolism. S. S. Z.

Relation between the Pancreas and the Carbohydrate Metabolism of Muscle. Effect of Extracts from the Gland on Lactic Acid Production *in vitro*. D. L. FOSTER and C. E. WOODROW (*Biochem. J.*, 1924, **18**, 562—574).—The pancreas contains a factor capable of causing marked inhibition in the lactic acid production of chopped muscle. This factor is not identical with trypsin or insulin, and is probably not antiglyoxalase. A method is described for making a stable preparation of the pancreas with all its enzymes intact, and details are given for making an extract of this preparation with 70% alcohol which contains the inhibitory factor in high concentration. S. S. Z.

Behaviour of β-Glucose in the Human Body and the Nature of the Glucose in Serum. S. J. THANNHAUSER and M. JENKE (*Münch. med. Woch.*, 1924, **71**, 196—198; from *Chem. Zentr.*, 1924, i, 1687).—Intravenous injection of β-glucose had the same effect on the blood-sugar curve and the excretion of sugar in the urine as αβ-glucose. The elimination of acetone in diabetes is not diminished to the same extent by β-glucose as by αβ-glucose. β-Glucose is probably a stage in the degradation of sugar. G. W. R.

Type of Sugar Excreted in the Urine of Normal Persons. K. TALLERMAN (*Biochem. J.*, 1924, **18**, 583—585).—The sugar excreted in the urine of the normal subject as a result of an injection of phloridzin is not γ-glucose, but the ordinary αβ-variety. Sugar of the same nature is found in the urine of diabetics after such an injection. γ-Glucose is therefore unlikely to be present in normal blood. S. S. Z.

Physiological Testing of Insulin Preparations. H. PÉNAU and H. SIMONNET (*J. Pharm. Chim.*, 1924, **29**, 473—481; cf. *B.*, 1924, 74).—Exception is taken to certain details of the Canadian physiological unit for insulin, and a modified test is described. W. T. K. B.

Insulin from the Cod Fish. Direct Application of Picric Acid to Islet Tissue. H. W. DUDLEY (*Biochem. J.*, 1924, **18**, 665—668).—The islet tissue of the cod contains, weight for weight, about ten times as much insulin as mammalian pancreas. The insulin can be obtained by treating the tissue directly with picric acid and then extracting the insulin-containing picrate with aqueous acetone and converting the picrate into a soluble hydrochloride as previously described by the author. The islet tissue of the cod collected from fish caught at varying intervals up to 24 hours previously yielded 13·1 rabbit units per g. of tissue. S. S. Z.

Preparation of Insulin. M. Somogyi, E. A. Doisy, and P. A. Shaffer (*J. Biol. Chem.*, 1924, **60**, 31—58; cf. *ibid.*, 1923, **55**, 31).—The activity of purified preparations of insulin from ox pancreas is associated always with a single, fairly well-characterised protein and probably is a property of this protein. "Insulin-protein" is relatively insoluble at a reaction of about p_H 5. Crude insulin contains, in addition, two other "isoelectric-proteins" which are inactive, one with optimum precipitation, in absence of salts, at p_H 7 or 8, and the other at p_H 4. In the pancreas extracts, there is also an "alcohol-protein," readily soluble in alcohol up to 80% and insoluble in higher concentrations, which is not precipitated on adjusting the reaction, but tends to interfere with the precipitation of "insulin-protein."

The solubility relationships, in presence and in absence of salts, of "insulin-protein" and the associated inactive proteins and the choice of acid for extraction, having been studied, a simplified method for the separation of active insulin has been worked out. Data are given illustrating the activity of different preparations. C. T. G.

Chemical Reactions of Insulin. C. H. Best and J. J. R. Macleod (*Amer. J. Physiol.*, 1923, **63**, 390—391).—Insulin, when free from protein, does not respond to any of the colour reactions for the latter, or for adrenalin. It is not appreciably affected by moderate heat in solution of p_H 5—6; it may be heated on a boiling water-bath for 10 minutes, but is destroyed by actual boiling for 3 minutes. Insulin is absorbed from acid solution by kaolin, charcoal, etc.; it could not be shown to dialyse through a collodion membrane. The potency of insulin preparations is greatly reduced by passage through a Berkfeld filter. Insulin preparations do not contain proteolytic enzymes. A. A. E.

Chemistry of Amino-acid Deamination. W. R. Fearon and E. G. Montgomery (*Biochem. J.*, 1924, **18**, 576—582).—Cyanic acid is an important factor in the production of urea and in the maintenance of neutrality in the organism, since it is shown that the acid is formed during the oxidative deamination of glycine, sarcosine, and alanine and that it is an intermediate product of α-deamination of glycine. S. S. Z.

Biochemistry of Experimental Tetany. Urinary and Muscle Creatine in Guanidine and Parathyroid Tetany with and without Calcium Treatment. A. Palladin and L. Griliches (*Biochem. Z.*, 1924, **146**, 458—466).—In experimental guanidine and parathyroid tetany, muscle creatine is increased and appears in the urine, whilst the excretion of creatinine is unaffected or but slightly increased. A direct relationship between muscle creatine and urinary creatine and creatinine is inferred. The abolition of tetanic symptoms by injection of calcium salts into rabbits, previously treated with guanidine, arrests the excretion of creatine and restores muscle creatine to normal limits. The increase of the latter in tetany is not ascribed to its increased formation from guanidine (cf. Paton, *Quart. J. Expt. Physiol.*, 1916, **10**),

since if calcium be administered simultaneously with guanidine the muscle creatine is not increased. J. P.

Sulphur Metabolism of the Dog. II. Constancy of the Relative Output of Ethereal Sulphate and of Neutral Sulphur after Oral Administration of Halogen-substituted Benzenes. T. S. HELE (*Biochem. J.*, 1924, **18**, 586—612).—Chlorobenzene administered by the mouth has an approximately constant quantitative effect on the sulphur metabolism of the dog. The "extra" ethereal sulphate bears a constant proportion to the "extra" neutral sulphur (about 2 to 3). This ratio may be altered by repeated doses of chlorobenzene if no cystine or sodium sulphate is given at the same time. The simultaneous oral administration of these latter compounds alone does not alter the ratio. The ratio of "extra" free phenol to "extra" total phenol also appears to be constant. There is no increase of free or conjugated phenols in the fæces after administration of chlorobenzene. The action of bromobenzene is similar to that of chlorobenzene. The oral administration of cystine always produces a small rise in the output of neutral sulphur. A rise in the protein intake may produce a considerable rise in the output of neutral sulphur. Guaiacol seems to have a slight toxic effect on sulphur metabolism. S. S. Z.

(Biological) Action of Sulphur. A. HOTTINGER (*Schweiz. med. Woch.*, 1923, **53**, 429—432; from *Chem. Zentr.*, 1924, i, 1826—1827).—A theoretical discussion of the rôle of sulphur and sulphides in biological oxidations and reductions. G. W. R.

Formation of Ethereal Sulphates. G. J. SHIPLE, J. A. MULDOON, and C. P. SHERWIN (*J. Biol. Chem.*, 1924, **60**, 59—67).—The feeding of bromobenzene, phenol, or *p*-chlorophenol to a pig maintained on a carbohydrate diet in a condition of endogenous nitrogen catabolism definitely increased the output of ethereal sulphates in the urine. Sodium sulphate, fed with the aromatic poisons, did not cause any further increase in ethereal sulphates; with phenol and bromobenzene there was actually a decrease. Cystine, given with phenol, caused an increase beyond that obtained with phenol alone, whilst cystine with bromobenzene or *p*-chlorophenol caused a marked decrease. Ethereal sulphates are therefore not formed simply at the expense of inorganic sulphates: the sulphur required must come from the tissues, presumably from tissue-cystine, although if cystine be present in the diet, it may be utilised. It is thought that when ethereal sulphates are formed from endogenous sulphur, the phenolic poison is first linked to an intermediary product of the metabolism of tissue-cystine and the whole eventually oxidised to the sulphate stage. If exogenous cystine is available, a complex analogous to *p*-bromophenylmercapturic acid may be formed and either excreted as such or oxidised to a sulphate. C. T. G.

Influence of Salts on Metabolism. II. Blood-sugar and Liver Glycogen. M. HÄNDEL (*Biochem. Z.*, 1924, **146**, 438—445).—Withholding of cell salts from the dietary of rats produces

a slight diminution in liver glycogen and a slight increase in blood-sugar. The addition of potassium has no appreciable effect, whilst calcium produces a slight increase in blood-sugar, but has no influence on the liver glycogen. The latter is likewise not affected by the addition of phosphates, which, however, produce a normal blood-sugar value. J. P.

Influence of Variations in the Sodium–Potassium Ratio on the Nitrogen and Mineral Metabolism of the Growing Pig. M. B. Richards, W. Godden, and A. D. Husband (*Biochem. J.*, 1924, **18**, 651—660).—The addition of sodium chloride or sodium citrate to a ration of cereal grain fed to a growing pig leads to increased assimilation and retention of nitrogen, calcium, and phosphorus. The increase of sodium salts in the ration causes increased excretion of potassium in the urine, which is, however, counterbalanced by the diminution of this element in fæcal excretion, and the balance is therefore normal. S. S. Z.

Mechanism of Acidosis in Anæsthesia. R. L. Stehle and W. Bourne (*J. Biol. Chem.*, 1924, **60**, 17—29).—A study of the relation between ether anæsthesia and increased excretion of phosphoric acid. C. T. G.

Classification and Grouping of Vitamins. W. Tönnis (*Z. physiol. Chem.*, 1924, **136**, 89—104).—In mice and rats, normal growth and duration of life are observed only when the diet comprises sources of all three vitamins, *A*, *B*, and *C*. The simultaneous administration to avitaminosed animals of two vitamins has a definite improving effect on the growth curve—*A* and *B* exerting a more marked effect than *A* and *C*—only during the early stages of avitaminosis. Alcoholic and weakly acidic extracts of yeast produce in adult rats, in addition to the curative effect on the paresis due to lack of vitamin-*B*, an increase in body-weight, an effect which is also shown by the extracted yeast. The presence of the supposed vitamin-*D* in yeast is therefore not confirmed. Alcoholic and aqueous yeast extracts exert no effects on the growth of young rats and mice which are not also shown by the extracted yeast itself, from which it is concluded that no evidence is forthcoming in support of the possible separation of the water-soluble growth vitamin from the anti-beri-beri vitamin, and the general conclusion is drawn that only the three vitamins, *A*, *B*, and *C*, exist. J. P.

Association of Manganese with Vitamins. J. S. McHargue (*J. Agric. Res.*, 1924, **27**, 417—424).—Manganese has been shown (cf. A., 1922, i, 906) to be an essential element in plant economy. In the animal body it is found most abundantly in the liver, kidney, and pancreas. The pericarp and germ of rice, barley, and wheat contain considerable amounts of manganese, which is largely removed during the polishing and milling processes. Cod-liver tissue, fish roe, the yolks of eggs, tomatoes, oranges, and lemons are relatively rich in manganese, whilst purified cod-liver oil and the whites of eggs contain negligible amounts. Colostrum is much

richer in manganese than milk. The fact that it is found in largest quantities in those plant- and animal-tissues which show the greatest vitamin potency suggests the existence of a relationship between manganese and these vital factors. E. M. C.

Preparation of a Crystalline Picrate having the Antineuritic Properties of Vitamin-*B*. A. SEIDELL (*U.S. Public Health Rep.*, 1924, 294—299; cf. Bertrand and Seidell, *Bull. Soc. Chim. biol.*, 1923, **5**, 794).—The mixture of picrates, previously described as resulting from the treatment of an aqueous-alcoholic extract of yeast with methyl-alcoholic picric acid, can be separated to some extent by repeated extraction with acetone. From the acetone-soluble portion there was obtained a picrate crystallising in reddish-yellow flakes, m. p. (decomp.) below 160°. A daily dose of 2 mg. of this picrate is sufficient to protect pigeons against loss of weight on a diet of polished rice. The residue from the acetone extraction crystallises in pale yellow rods and prisms, m. p. 202°, and is physiologically inert. Both picrates, on combustion, give figures corresponding with the formula $C_6H_{18}O_2N_3,C_6H_2(OH)(NO_2)_3$. C. R. H.

Antiscorbutic Fraction of Lemon Juice. II. S. S. ZILVA (*Biochem. J.*, 1924, **18**, 632—637).—When decitrated lemon juice is fermented in order to remove the sugar an active solution is obtained. On concentrating such a solution and precipitating with absolute alcohol, further non-active matter is removed in the precipitate. When such purified solution is treated with basic lead acetate, the entire antiscorbutic vitamin is precipitated. On removing the lead and bringing the solution up to its original volume, a preparation is obtained which contains the entire antiscorbutic activity of the original lemon juice, but only 0·03—0·07% of solids. Basic lead acetate also brings down the vitamin entirely in unfermented decitrated lemon juice, but in this case more extraneous matter (sugar, etc.) is also precipitated with it. These active preparations reduce ammoniacal silver nitrate in the cold and decolorise potassium permanganate. A new method for the removal of acids and other non-active matter from lemon juice without vitiating its antiscorbutic activity is described. S. S. Z.

Reducing Properties of Antiscorbutic Preparations. S. J. B. CONNELL and S. S. ZILVA (*Biochem. J.*, 1924, **18**, 638—640).—The destruction of the reducing properties of antiscorbutic solutions observed by Zilva (see preceding abstract) by heat and by alkalinity in the presence of air does not proceed at the same rate as the inactivation of the vitamin by the same means. Further evidence is produced which shows that the modified Folin's reagent suggested by Bezssonnoff (this vol., i, 686, 789) for the detection of the antiscorbutic factor is untrustworthy. S. S. Z.

Differential Dialysis of the Antiscorbutic Factor. II. S. J. B. CONNELL and S. S. ZILVA (*Biochem. J.*, 1924, **18**, 641—646).—The diffusion of the antiscorbutic factor proceeds differently

from that of the sugar and the nitrogenous substances present in decitrated lemon juice. The antiscorbutic factor in swede juice and in lemon juice diffuses through membranes of the same permeability. There are indications that the size of the active molecule cannot be far removed from that of the hexoses. S. S. Z.

Antiscorbutic Value of Fresh and Canned English Tomatoes. E. M. Delf (*Biochem. J.*, 1924, **18**, 674—678).—Raw fresh juice of English tomatoes is not quite as effective an antiscorbutic as fresh orange- or lemon-juice. Bottled tomatoes stored for six months were found to have lost about two-thirds of their original activity. Canning causes a loss of nearly three-quarters of the original value. A further but smaller loss takes place after storage for about 4 years. Canned tomato purée retains only about one-seventh of its original activity. S. S. Z.

Creatine Content of Brain. V. J. Harding and B. A. Eagles (*J. Biol. Chem.*, 1924, **60**, 301—310).—The percentage of creatine in the brain as a whole is a constant for any individual species; it is always higher in the cerebellum than in the cerebral hemispheres; it is independent of the amount of creatine in the diet, and it is rapidly reduced by autolysis of the brain-tissue. C. R. H.

Isolation of Arachidonic Acid from Brain-tissue. L. G. Wesson (*J. Biol. Chem.*, 1924, **60**, 183—187).—Bromine is added in slight excess to the ether extract of ground brain-tissue previously dehydrated with acetone. The white precipitate is removed, digested at 37° for 24 hours with 50% alcohol containing 5% of hydrochloric acid, washed, and dried at 100°. Analysis shows this substance to be the octabromide of arachidonic acid. The yield is about 3·5 g. per kg. of wet brain-tissue. The compound may be debrominated by boiling an alcohol solution for about 4 hours with copper-coated zinc (if the ethyl ester is required, dry hydrogen chloride is passed slowly through the boiling alcohol solution for 1 hour); water is then added and the acid (or ester) extracted with ether. The free acid thus obtained has all the properties of arachidonic acid, and there is little reason to suspect that it is different from the acid present as glyceride in the tissues. C. T. G.

Gelatinolytic Liver Enzyme. Tsou-Hia Hsü (*Biochem. Z.*, 1924, **146**, 540—544).—The gelatin-liquefying enzyme present in liver extracts (Hata, A., 1909, ii, **416**) may be precipitated from fresh preparations, but not from old extracts, by ammonium sulphate. Various attempts to isolate the enzyme by precipitation with uranyl acetate, and by separation of the accompanying proteins by means of cholesterol, are described. J. P.

Hippuric Acid Balance in Renal Diseases. J. Snapper and A. Grünbaum (*Klin. Woch.*, 1924, **3**, 101—104; from *Chem. Zentr.*, 1924, i, 1689).—After administration of 3—5 g. of sodium hippurate

to healthy men, only traces of hippuric acid were found in the blood, whilst in certain renal diseases 4—40 mg. % were found. Both diseased and healthy kidneys produced hippuric acid, but in the former case it was eliminated with difficulty.

G. W. R.

Extractives of Ox Spleen. J. HAGIHARA (*Z. physiol. Chem.*, 1924, **136**, 232—234).—A hot-water extract of ox spleen, after removal of the protein, gave no crystallisable substances in the arginine, histidine, and lysine fractions. O. O.

Nuclein Substance of the Spleen. J. HAGIHARA (*Z. physiol. Chem.*, 1924, **135**, 294—316).—Extracts of dried ox spleen with 10% sodium chloride, yielded, on treatment with copper sulphate or calcium chloride, precipitates with a phosphorus : nitrogen ratio of 1 : 1·5 to 1 : 2·5. On hydrolysis with 5% sulphuric acid and precipitation with ammoniacal silver nitrate, the presence of purine bases could not be established with certainty, the supposed guanine fraction giving nitrogen values which were too low. Guanylnucleic acid was not detected in the original dried gland. Various other methods of precipitating nucleic acids were applied to the preparations of the spleen, but the material obtained showed a variable composition and no very definite conclusions are drawn. J. P.

Significance of Ions in Muscular Function. G. EMBDEN and E. LEHNARTZ (*Z. physiol. Chem.*, 1924, **134**, 243—275).—A comparison was made of the effects of the sodium salts of various acids on the breakdown of lactacidogen in freshly-chopped muscle, to give lactic and phosphoric acids. In this respect, the ions arrange themselves according to the Hofmeister series, the greatest effect being obtained with thiocyanate and iodide and scarcely any with sulphate and tartrate. Sodium citrate and, especially, sodium fluoride, bring about the reverse reaction, viz., a disappearance of inorganic phosphate and synthesis of lactacidogen. The power of the different ions to stimulate breakdown of lactacidogen is found to correspond with their power to restore activity to a frog's muscle which has been inhibited by keeping in sucrose solution or otherwise.

C. R. H.

Significance of Ions in Muscle Functions. II. Influence of Sodium Fluoride Solutions on Lactic Acid Formation in Frog-muscle Pulp. G. EMBDEN, A. ABRAHAM, and H. LANGE (*Z. physiol. Chem.*, 1924, **136**, 308—312).—Sodium fluoride in concentrations of *M*/100, *M*/10, and *M*/1 favoured the formation of lactacidogen but inhibited the lactic acid formation almost completely. At low concentrations (*M*/1000—*M*/10,000), the formation of lactacidogen is diminished and lactic acid formation increased. When the sodium fluoride solutions contained 2% of sodium hydrogen carbonate similar relations held, but the extent to which lactacidogen synthesis or lactic acid formation occurred was usually greater.

O. O.

Hydrolysis of Protein by a Heat-stable Catalyst Present in Muscle. W. M. CLIFFORD (*Biochem. J.*, 1924, **18**, 669—673).—Cod muscle contains a heat-stable catalyst which hydrolyses protein. S. S. Z.

Possible Significance of Hexosephosphoric Esters in Ossification. II. The Phosphoric Esterase of Ossifying Cartilage. R. ROBISON and K. M. SOAMES (*Biochem. J.*, 1924, **18**, 740—754).—The phosphoric esterase described by Robison which is present in bone and ossifying cartilage is also present in equally high degree in teeth, especially in those of very young animals. This enzyme also hydrolyses ethyl butyrate and triacetin, but not olive oil. It is distinct from the esterase of pancreas, which is relatively inactive towards phosphoric esters. The optimum reaction of the enzyme is p_H 8·4—9·4—a reaction favourable for the precipitation of tertiary calcium phosphate and calcium carbonate. The deposition of fresh calcium phosphate has been demonstrated in bones taken from rachitic rats in solutions of calcium hexosemonophosphate or calcium glycerophosphate at 37° at the above reaction. It is argued that the enzyme is secreted in the region of the osteoblasts and hypertrophic cartilage cells and is actively concerned in ossification. It is suggested that the reaction of the tissue fluid in the region of ossification is rendered more alkaline than the blood by some mechanism, thereby increasing the activity of the enzyme, and favouring the deposition of both calcium phosphate and carbonate. S. S. Z.

Possible Significance of Hexosephosphoric Esters in Ossification. III. Action of the Bone Enzyme on the Organic Phosphorus Compounds in Blood. H. D. KAY and R. ROBISON (*Biochem J.*, 1924, **18**, 755—764).—The acid-soluble organic phosphorus compounds present in the blood of various animals consist of at least two phosphoric esters, one of which is rapidly hydrolysed by the enzyme of ossifying cartilage (see preceding abstract), whilst the other is very resistant to the action of this enzyme. Both esters are hydrolysed by boiling with 0·2*N*-sulphuric acid. A method has been worked out by which the respective amounts of these esters may be determined and results of such determinations are given for the blood of human adults and children, and of rats, rabbits, and cockerels. The amount of ester hydrolysed by the bone enzyme varies between 14 and 36% of the total acid-soluble phosphorus. This ester is present almost entirely in the corpuscles. Attempts to demonstrate the presence of hydrolysable esters in the plasma lead to inconclusive results. There are indications that the esters are able to diffuse from the corpuscles to the plasma. The phospholipins present in the blood are not hydrolysed by the bone enzyme. S. S. Z.

Cholesteryl Palmitate, a Constituent of Corpus Luteum. M. C. HART and F. W. HEYL (*J. Amer. Pharm. Assoc.*, 1924, **13**, 17—22).—Dried corpus luteum contained 4·5—5·4% of ash.

Cholesteryl palmitate, potassium stearate, free fatty acids, and possibly cholesteryl stearate were identified in the acetone extract.
CHEMICAL ABSTRACTS.

Microchemical Detection of a Nucleic Acid of the Thymonucleic Acid Type and the Selective Coloration Dependent Thereon in Microscopic Preparations. R. FEULGEN and H. ROSSENBECK (*Z. physiol. Chem.*, 1924, **135**, 203—248).—A colour test called the "nucleal reaction" is described, whereby the presence of nucleic acids of the type of thymonucleic acid may be demonstrated in micro-preparations by the development of a red colour after these have been submitted to mild hydrolysis (4 minutes at 60° with 0·1*N*-hydrochloric acid), followed by treatment with fuchsin–sulphurous acid. The reaction is given by nucleic acids containing a hexose residue, such as thymus-nucleic acid, but not by the nucleic acids containing a pentose such as yeast-nucleic acid and triticonucleic acid. Nevertheless, certain of the higher plants (wheat embryos, bulbous plants) give a positive reaction, and it is inferred that in these cases a hexose acid must be present in addition to the well-established pentose acid. This is paralleled by the occurrence in animal cells of such pentose nucleotides as inosinic and guanylic acids. The nuclei of ciliate protozoa (infusoria) give the nucleal coloration, but in still lower representatives of the class (trypanosomes) it is absent. Bacteria are also, like yeast-cells, "anucleal." Yeast-nucleic acid, typical of the lower plants, is regarded as being the primitive form of the substance; it becomes partly replaced in the higher plants by the "nucleal" acid, and the primitive form almost entirely disappears in the animal world, surviving only in the form of the pentose nucleotides. The nucleic material occurring in rye and responsible for the nucleal reaction in the higher plants has been isolated in an impure condition. It is rich in phosphorus and gives a marked reaction with fuchsin–sulphurous acid after mild hydrolysis just as does thymus-nucleic acid. J. P.

Mechanism of "Nucleal" Staining. I. Detection of Reducing Groups in the Nuclei of Partly Hydrolysed Micro-preparations. R. FEULGEN and K. VOIT (*Z. physiol. Chem.*, 1924, **135**, 249—252).—The nuclei of partly hydrolysed preparations of frog erythrocytes give a brown coloration, due to reduced colloidal silver when treated with a saturated aqueous solution of silver oxide. The reaction is not given by non-hydrolysed preparations. The presence of reducing groups liberated by hydrolysis of the nuclear material is inferred. J. P.

Mechanism of "Nucleal" Staining. II. Behaviour of the Nucleus of Partly Hydrolysed Microscopic Preparations to Magenta–Sulphurous Acid after Preliminary Treatment with Phenylhydrazine. R. FEULGEN and K. VOIT (*Z. physiol. Chem.*, 1924, **136**, 57—61).—The "nucleal" colour reaction (cf. preceding abstracts) is given by partly hydrolysed (4 mins. at 60° in 1·0*N*-hydrochloric acid) micro-preparations, but not after

these have been treated with phenylhydrazine acetate. Preparations treated with acid for 1 min., then with phenylhydrazine, and subsequently hydrolysed further, give the reaction, which is therefore ascribed to a chemical combination between magenta–sulphurous acid and the aldehyde groups liberated by separation of the purine residues of the nucleic acids during mild hydrolysis. J. P.

Iron Content of Nucleoproteins. T. TAKAHATA (*Z. physiol. Chem.*, 1924, **136**, 214—218).—The rôle of iron which occurs in the precipitate of nucleoproteins obtained with acetic acid from an aqueous extract of an organ is not quite clear. In analogy with the iron of the blood pigments, it may have some significance in oxidation processes or it may have a direct relation with the red blood-corpuscles and their genesis. It appears very doubtful whether the iron of the nucleoproteins can participate at all in oxidation processes. As nucleic acids are known to be free from iron and most proteins contain it only in traces, the iron content of different nucleoproteins has been examined. It is found that most extracts of different organs contain a sufficient amount of inorganic iron salts, a certain amount of which is precipitated with the nucleoprotein.
D. R. N.

Production of Ammonia and Urea in Autolysis. R. A. MCCANCE (*Biochem. J.*, 1924, **18**, 486—497).—The optimum hydrogen-ion concentration for the production of ammonia and urea by autolysis from spleen and kidney is p_H 6. When liver is employed in the winter the optimum p_H for ammonia production is the same but it is not so marked. The optimum for urea production lies in the region of p_H 5—5·5. During the summer, the ammonium curves are unchanged, but the production of urea at p_H 5—5·5 falls to a value often lower than that at p_H 6. When the tissues are autolysed in the presence of oxygen and hydrogen, the total nitrogen is always the same, and also the p_H. The ammonia is sometimes the same and sometimes slightly higher in the hydrogen filtrate. The urea is always very much greater in the hydrogen filtrate, and the amount of urea produced in an autolysis in hydrogen is the same as when the gas is not present during the process. Nitrogen and hydrogen give identical results. The production of ammonia is common to all autolyses; that of urea occurs only in certain organs. It is not produced in the case of mammalian pancreas (bullock, pig), lung, skeletal muscle (bullock), heart-muscle (sheep) or avian liver (hen). Ammonia and urea are formed by separate processes. Their precursors are discussed. An enzyme which forms part of the urea-producing system and is strongly inhibited by gaseous oxygen is described and discussed. S. S. Z.

Occurrence of Agmatine in Lower Animals. F. HOLTZ (*Z. Biol.*, 1924, **81**, 65—67).—An extract of the giant siliceous sponge, *Geodia gigas*, was found to contain agmatine, a base already known to occur in vertebrates and in some lower plants, but not hitherto found in any invertebrate. The substance was isolated as the picrate

from the arginine fraction of the extract. It was identified by the composition and properties of the picrate, chloroaurate, and carbonate. Arginine was not found in the extract of *G. gigas*.

C. T. G.

Occurrence of Trigonelline in the Animal World. F. Holtz, F. Kutscher, and F. Thielmann (*Z. Biol.*, 1924, **81**, 57—60).—Trigonelline, hitherto found only in plants, is now reported as occurring in the sea-urchin *Arbatia pustulosa*. The extract of 109·5 kg. of the animals was treated according to Kutscher's method (*Z. Nahr. Genussm.*, 1905, **10**, 528; A., 1906, ii, 562) and 13 g. of the gold salt of the alkaloid were isolated from the "lysine fraction." The alkaloid was identified by analyses and m. p. of the chloroaurate, chloroplatinate, chloride, and of the free base. Roeder's observation (A., 1914, i, 25) that the potassium ferrocyanide compound of trigonelline crystallises as red, lustrous prisms (the corresponding compound of glycine-betaine being white) was confirmed with trigonelline prepared from nicotinic acid and from sea-urchins.

The discovery of trigonelline in the animal world makes the occurrence of methylpyridinium hydroxide in crabs, sea-anemones, and other animals more easily intelligible, since this compound may be formed from trigonelline by addition of water and loss of carbon dioxide.

C. T. G.

Recognition of Arginine, Betaine, Choline, and Acanthine in the Embryos and Liver of the Spiny Dog-fish (*Acanthias vulgaris*). E. Berlin and F. Kutscher (*Z. Biol.*, 1924, **81**, 87—92).—The presence in various cold-blooded animals of certain "intermediate" products of metabolism such as betaines and methylpyridinium hydroxide, which normally occur in plants, has recently been demonstrated. From the aqueous extract of about 1 kg. of the embryos of the common dog-fish (*Acanthias vulgaris*), arginine, betaine (12 g.), and choline (0·5 g.) were isolated from the phosphotungstic precipitate, whilst from the filtrate from the latter was isolated about 1 g. of a substance, $C_{15}H_{22}O_4N_4$, m. p. 122—124°, for which the name *acanthine* is suggested. It does not give the biuret or tryptophan reactions, but gives Pauly's diazo-reaction.

Betaine and choline were also found in the liver of the dog-fish. The embryos contain 1·2% of betaine and the liver and muscle about 0·07%; similarly, young beetroots contain more betaine than the older plants, indicating that in both plants and animals the substance is formed in the early stages and utilised during growth.

C. T. G.

Changes in Chemical Composition of the Tissues of the Herring in Relation to Age and Maturity. J. R. Bruce (*Biochem. J.*, 1924, **18**, 469—475).—At any given stage of sexual maturity, the water, fat, and protein contents of the fresh muscle substance of the herring are dependent on age, the older fish containing a lower percentage of water and protein and a higher percentage of fat. This variation in composition with age resembles

that previously observed to be associated with the successive stages of sexual maturation. The metabolic demands of the growing gonads are made first on the fatty reserves of the liver. The muscular tissue is depleted only shortly before spawning. There are indications that the developing gonads have a high phosphorus requirement and that phosphatides play a part in the tissue changes and translocation associated with maturation. S. S. Z.

Culture of the Marine Diatom *Nitzschia closterium* (F.) *minutissima* in Artificial Sea-water. E. A. Peach and J. C. Drummond (*Biochem. J.*, 1924, **18**, 464—468).—This organism can grow and thrive in an inorganic culture medium, and does not require an organic substance specific to its growth. S. S. Z.

Occurrence of Lactase in the Alimentary Tract of the Chicken. T. S. Hamilton and H. H. Mitchell (*J. Agric. Res.*, 1924, **27**, 605—608; cf. following abstract, and Plimmer and Rosedale, A., 1922, i, 485).—Lactase is present in the crop, but absent from the proventriculus, the pancreas, and the intestines of normal chickens. E. M. C.

Utilisation of Lactose by the Chicken. T. S. Hamilton and L. E. Card (*J. Agric. Res.*, 1924, **27**, 597—604).—The lactose present in the whole or skim milk, whey, or buttermilk consumed by chickens will be completely absorbed. Lactose was utilised fairly completely in amounts up to 8 g. per hen per day, although such amounts invariably produced acute diarrhœa. Large amounts of uric acid interfere with the Munson-Walker-Bertrand method, but not with the Benedict method, for the determination of reducing sugars. E. M. C.

Reducing and Oxidising Reaction in Milk. P. Haas and B. Lee (*Biochem. J.*, 1924, **18**, 614—620).—Itate and peroxydase are not identical, since they can be partly separated. Itate does not oxidise nitrite directly. It forms a peroxide by acting on the acetaldehyde present, which in its turn is utilised by the peroxydase of the milk in oxidising the nitrite. Attempts to effect a similar oxidation of nitrite by a peroxydase of vegetable origin in the presence of hydrogen peroxide have so far been unsuccessful. S. S. Z.

Fission and Synthesis of Esters by Lipase from the Lacteal Glands and from Milk. A. I. Virtanen (*Z. physiol. Chem.*, 1924, **137**, 1—13).—An investigation of the fission and synthesis of esters by the expressed juice and the glycerol extract of the lacteal glands of cattle. The lipolytic properties of these glands are very feeble. In the quantitative experiments only the glycerol extract was used, and concordant results were obtained only when p_H was maintained constant throughout. Under these conditions the hydrolysis of ethyl butyrate at 40° follow the course of a unimolecular reaction. In a series of experiments in which p_H varied from about 8·7 to about 5, the velocity of hydrolysis decreased with decrease

in p_H, finally ceasing at a value somewhat below 5. This cessation was not due to the destruction of the lipase by the acidity of the solution. Attempts to esterify butyric acid with glycerol failed, but the synthesis of ethyl butyrate was effected. Synthesis occurs at p_H values up to about 4, but beyond this value the reaction ceases. Whole milk acted hydrolytically at p_H 8·8. B. F.

Secretion of Bile. III. E. NEUBAUER (*Biochem. Z.*, 1924, **146**, 480—485).—In continuation of previous work (*ibid.*, 1922, **130**, 556), it is shown that dehydrodeoxycholic acid is a powerful cholagogue, somewhat more active than deoxycholic acid, whilst in its hæmolytic action it is somewhat weaker than both deoxycholic and cholic acids. In 1·5% aqueous solution sodium dehydrodeoxycholate has a surface tension higher than that of sodium deoxycholate and cholate, and lower than that of sodium dehydrocholate. Dehydrodeoxycholic acid is less toxic in its cardiac effects than deoxycholic acid. It is concluded that hæmolytic and toxic action in the bile acid group increases with surface activity, whilst the latter is not related to cholagogic properties. J. P.

Blood and Spinal Fluid. II. Calcium, Magnesium, and Phosphorus. N. G. BARRIO (*J. Lab. Clin. Med.*, 1923, **9**, 54—56).—The spinal fluid contains (in mg. per 100 c.c.) 4·6—6·1 of calcium, 1·5—2·7 of inorganic phosphorus, and 1·4—6·1 of magnesium. The concentrations are, respectively, 50%, 50%, and 125% of those of the blood-serum. CHEMICAL ABSTRACTS.

Analysis of Liquid Produced in a State of General Oedema. R. FABRE (*J. Pharm. Chim.*, 1924, **29**, 484—485).—The pale yellow, feebly acid liquid (d^{15} 1·009) contained, per litre, protein 1·2 g., urea 0·92 g., uric acid nitrogen 0·43 g., combined ammonia 0·034 g., ammoniacal nitrogen 0·028 g., total nitrogen 0·66 g., and sodium chloride 5·73 g.; ratio of uric acid nitrogen to (total—protein) nitrogen, 0·85. The blood, at the time of puncturing, contained 0·89 g. of urea per litre. W. T. K. B.

Excretion of Uric Acid in the Urine of Dogs. P. MEDERHOFF (*Z. physiol. Chem.*, 1924, **137**, 85—88).—After feeding on potato until the urine was free from uric acid, pure uric acid was mixed with the diet of a dog; no uric acid was excreted in the urine until the administration of the pure substance reached 2 g. per day. With larger doses, the quantity excreted increases with the dose. When meat was substituted for potato in the diet, the excretion of uric acid was somewhat greater than before; it is shown that this is not due to the purine content of meat. It is concluded that the power of dogs to decompose uric acid is quite low, and hence that the amount of purine derivatives which may be formed intermediately in the course of the metabolism of the dog is not very large. B. F.

Significance of Determinations of Uric Acid in Urine, Particularly in Gout, Related Diseases, and Uric Acid Diathesis. M. WEINTRAUT (*Arch. Pharm.*, 1924, **262**, 48—52).—The results obtained in the determination of uric acid in the urine

are mainly of significance when compared with the amount of acid phosphates present (Zerner's coefficient) and with the urea (coefficient of uric acid diathesis); their clinical significance is discussed.

G. M. B.

Fat Excretion. II. Quantitative Relations of the Fæcal Lipoids. W. M. SPERRY and W. R. BLOOR (*J. Biol. Chem.*, 1924, **60**, 261—287).—An exhaustive fractionation of the lipoid content of the fæces of cats and dogs under various dietary conditions showed that the total lipoid excretion is almost as great on a fat-free diet as on one rich in fats; it is less on a "sham-feeding" diet of agar and bone-ash. The relationships between the individual fractions and the total lipoid are not markedly affected by changes in the diet except that an increase in the intake of fatty acids calls forth an increase in the excretion of fatty acids of the same nature. There is, in general, a close resemblance between the lipoid material of the fæces and that found in the blood. The authors suggest that the fat excreted in the fæces does not originate directly from the fat of the food, but represents an excretion of lipoid materials from the blood.

C. R. H.

Presence of Pyruvic Acid in the Contents of the Intestine. A. BERTHELOT and G. AMOUREUX (*Bull. Soc. Chim. biol.*, 1924, **6**, 338—339).—Pyruvic acid was found in the fæces of a subject whose intestinal flora was rich in *Bacillus aminophilus* and whose food for several years had consisted solely of fruit, vegetables, starchy materials, sugar, butter, and a little milk. Before the experiment, a quantity of potatoes was taken in addition to the usual ration and, in the evening, 8 g. of precipitated chalk. Pyruvic acid was also detected in the contents of the small intestine of a guinea-pig fed for 4 days on bread and potatoes treated with a rich culture of *B. aminophilus*, but not in the large intestine, where it is no doubt utilised by bacteria, thus accounting for its absence from normal fæces.

C. T. G.

Minimal Lethal Doses of Lead Salts Intravenously Injected. L. SCREMIN (*Arch. expt. Path. Pharm.*, 1924, **101**, 207—217).—From experiments on the intravenous injection into rabbits of lead nitrate, chloride, iodide, sulphate, carbonate, sulphide, and phosphate (the first two in true solution, the remainder in colloidal solution), it was found that the toxicity of the salts diminished in the above order, which is also the order of diminishing solubility. The salts fall into three groups, the first consisting of the nitrate, chloride, and iodide (and acetate), all of which are very toxic. Of the remainder, all except the phosphate are in an intermediate group of moderate toxicity; the phosphate is only slightly toxic.

H. J. P.

Influence of Phosphorus Poisoning on Muscle Creatine and on Creatine–Creatinine Excretion. A. PALLADIN and A. KUDRJAWZEWA (*Z. physiol. Chem.*, 1924, **136**, 45—56).—Phosphorus-poisoned rabbits show an increase in muscle creatine and an increased creatinine excretion with associated creatinuria. This is correlated

with a diminution in lactacidogen in the muscle, with a hypoglycæmia, and with a general diminution in carbohydrates.

J. P.

Viscosity and Toxicity of Arsphenamine [Salvarsan] Solutions. C. VOEGTLIN, J. M. JOHNSON, and H. DYER (*U.S. Public Health Rep.*, 1924, 179—195).—Dilute solutions of salvarsan on keeping undergo a progressive diminution in toxicity; at the same time there is a diminution in the viscosity of the solution. Investigation of a large number of samples, both of the hydrochloride and of the di-sodium salt, showed that this relationship between viscosity and toxicity is a general one. C. R. H.

Pharmacology of Benzyl Alcohol and Esters. I. Effect of Benzyl Alcohol, Acetate, and Benzoate (per os). II. (Intravenously.) C. M. GRUBER (*J. Lab. Clin. Med.*, 1923, **9**, 15—33, 92—112).—The action of benzyl acetate and benzoate is not dependent on their hydrolysis to benzyl alcohol.

CHEMICAL ABSTRACTS.

Hypoglycæmic Action in Bases of the Choline Group. A. MADINAVEITIA and S. HERNÁNDEZ (*Anal. Fís. Quím.*, 1924, **22**, 168—173).—The ethyl ester of betaine produces hyperglycæmia in rabbits. G. W. R.

Ethyl*iso*amylbarbituric Acid, an Anæsthetic without Influence on Blood-sugar Regulation. J. H. PAGE (*J. Lab. Clin. Med.*, 1923, **9**, 194—196).—Ethyl*iso*amylbarbituric acid has little or no influence on blood-sugar in amounts sufficient to produce surgical anæsthesia. CHEMICAL ABSTRACTS.

[**Physiological Effect of Iodine Solutions.**] E. RUPP.—(See ii, 562.)

Toxicity of Copper Sulphate to the Spores of *Tilletia tritici* (Bjerk.), Winter. F. N. BRIGGS (*Univ. Calif. Pub. in Agric. Sciences*, 1923, **4**, 407—412).—The germination of spores of *Tilletia tritici* was inhibited by 0·002*N*-copper sulphate but was not affected by solutions more dilute than 0·0004*N*. E. M. C.

Organic Mercury Compound with Powerful Germicidal Properties. G. W. RAIZISS and M. SEVERAC (*J. Lab. Clin. Med.*, 1923, **9**, 71—80).—4-Nitro-3 : 5-diacetoxydimercuri-*o*-cresol is a powerful germicide and has a high mercuric chloride index; it is a non-irritant and has low toxicity when given intramuscularly. It does not precipitate proteins in 1 : 200 concentration.

CHEMICAL ABSTRACTS.

Antiseptic Action of Compounds of the *apo*Cyanine, Carbocyanine, and *iso*Cyanine Series. C. H. BROWNING, J. B. COHEN, S. ELLINGWORTH, and R. GULBRANSEN (*Proc. Roy. Soc.*, 1924, **B**, **96**, 317—333).—In general, the compounds tested had a more powerful antiseptic effect on *Staphylococcus aureus* than on *Bacillus coli*, and there appears to be no relation between the chemical nature of the substances and their antiseptic effect. In the *apo*cyanine and

*iso*cyanine series, the introduction of amino groups tends to diminish rather than to enhance the antiseptic effect. The addition of side-chains to the quinoline fraction of the molecule in the *iso*cyanine series, in contrast to their presence in the 2-methylquinoline fraction, reduces the antiseptic effect. O. O.

Antiseptic Action of Benzoic Acid, Salicylic Acid, Cinnamic Acid, and their Salts. H. I. WATERMAN and P. KUIPER (*Rec. trav. chim.*, 1924, **43**, 323—325).—The growth of *Penicillium glaucum* in liquid media at room temperature was greatly hindered by 0·05—0·1% of benzoic acid (p_H 4·4—4·0), 0·05—0·06% of cinnamic acid (p_H 4·8—4·4) or 0·04—0·06% of salicylic acid (p_H 4·8—3·4). Much larger concentrations of the sodium salts (p_H 6·5—6·4) were without much influence. The inhibiting action is not due to hydrogen-ion concentration, but is explained by the Meyer-Overton lipoid theory, which attributes antiseptic action to undissociated molecules of the organic acid (cf. Vermast, A., 1922, i, 406). The checking of growth by borax at a concentration (on anhydrous salt) of 0·2—0·3% (p_H 8·2—8·4) is, however, undoubtedly due to hydroxyl ions, since it occurred at the same p_H with sodium hydroxide or carbonate. E. H. R.

Influence of Hydrogen-ion Concentration in the Presence of Salts on the Growth of *Gibberella Saubinetii*. H. LUNDEGÅRDH (*Biochem. Z.*, 1924, **146**, 564—572).—The growth of cultures of *Gibberella*, which is increased at a given hydrogen-ion concentration by the presence of salts, shows a maximum at p_H 6·8 in the presence of phosphate, whilst in the presence of calcium the maximum occurs at p_H 4·7. An antagonism between hydrogen- and calcium-ion concentrations is inferred. Calcium diminishes the inhibiting action of magnesium on the fungus. Ammonium salts give a reaction similar to that of calcium but less well marked, whilst aluminium is very toxic. J. P.

Synthesis of Starch from Sugar by Bacteria. E. C. GREY (*Biochem. J.*, 1924, **18**, 712—715).—Bacteria synthesise starch abundantly from dextrose. This formation of the polysaccharide can only be observed at a very early stage of the fermentation; the synthetic period in this investigation was found to be over in about 40 hours. S. S. Z.

Oxygen Uptake of Bacteria. A. B. CALLOW (*Biochem. J.*, 1924, **18**, 507—518).—The oxygen uptake of spore-forming and non-spore-forming aërobic bacilli, spore-forming anaërobic bacilli, and aërobic cocci was studied. The organisms were washed free from culture medium, emulsified in sterile buffer solution, p_H 7·6, and investigated for the oxygen uptake at 22° in Barcroft's micro-respirometer. Hydrogen-ion concentration had no appreciable effect on the oxygen uptake. Bacteria grown on agar or dextrose tryptic broth gave the same oxygen uptake as when grown on tryptic broth. *Bacillus pyocyaneus*, *B. fluorescens*, *B. prodigiosus*, *B. alcaligenes*, *B. proteus*, *B. coli*, Timothy grass bacillus, *B. megatherium*, *B. subtilis*, *Staphylococcus aureus*, and *Sarcina aurantiaca*, took up large

amounts of oxygen (5—25 c.c. per hour per g. of dry weight) at a steady rate. *B. alcaligenes*, *S. aureus*, and Timothy grass bacillus took up nearly as much oxygen when dried in a vacuum and emulsified in a buffer solution as before drying. *B. pyocyaneus*, on the other hand, took up oxygen after being dried at a much reduced rate. The aërobe *S. acidi lactici*, like the anaërobe *B. sporogenes*, took up only a minute amount of oxygen, at a rapidly decreasing rate. The presence of catalase did not alter the oxygen uptake of *S. acidi lactici* or *B. sporogenes*. S. S. Z.

Equilibria between Succinic, Fumaric, and Malic Acids in the Presence of Resting Bacteria. J. H. Quastel and M. D. Whetham (*Biochem. J.*, 1924, **18**, 519—534).—Resting cells (*i.e.*, a saline emulsion of the organism grown for 2 days) of *Bacillus coli* and *B. pyocyaneus*, possess an enzyme, similar to that present in muscle, which is capable of bringing about a reduction of methylene-blue in presence of sodium succinate with the formation of fumaric acid. This reaction is reversible. The effect of varying p_H on the times of reduction is a summation of the effect on the physical structure of the organism and the effect on the chemical reaction. Below p_H 5·0 no apparent reduction can be obtained and the organism appears to be coagulated. The velocity of reduction increases rapidly with increase of p_H from 6·0 to 9·0 but not above this figure. The effect of heat on the reaction at constant p_H is also a summation of two superimposed effects as mentioned above. The reduction velocity increases with increase of temperature. The temperature coefficient between 30° and 60° is 2·1. The temperature of 45° is very suitable for a high velocity of reduction without risk of injury to the organism. The rate of reduction is roughly directly proportional to the concentration and the organism present. The rate of decolorisation of the methylene-blue and the equilibrium constant of this equation are also worked out. The reversible equilibrium fumaric acid $\rightleftharpoons$ *l*-malic acid exists in presence of resting organism, fumaric acid in small quantities having been isolated after the action of the resting organism on *l*-malic acid. It has been shown that fumaric acid readily absorbs oxygen in presence of resting organisms although it will not donate hydrogen to methylene-blue.

S. S. Z.

Effect of Oxygen Supply on the Metabolism of *Bacillus coli communis*. M. Stephenson and M. D. Whetham (*Biochem. J.*, 1924, **18**, 498—506).—The carbon dioxide output and oxygen uptake of *B. coli* on a dextrose inorganic medium were studied. The organism is almost anaërobic during the early stages of dextrose breakdown. In an atmosphere of oxygen there is an increase in carbon dioxide output and a larger increase in oxygen uptake, which is not associated in the early stages of the experiment with increased utilisation of dextrose. Metabolism continues longer in oxygen than in air, the limiting hydrogen-ion concentration not being reached so soon. The increase of gaseous exchange with increase of oxygen pressure is attributed to the action on some acid degradation product of dextrose; this is supported by the

observation that the disappearance of lactic acid (as the ammonium salt) with the production of carbon dioxide is greatly increased with increased oxygen tension. The growth of the organism does not take place on lactic acid under anaërobic conditions. Succinic and acetic acids and glycerol are also suitable sources of carbon for *B. coli* in air but not under anaërobic conditions. S. S. Z.

Use of Clark and Lubs Indicators for the Detection of Acid Production by the Colon–Typhoid Group. P. A. TETRAULT (*Proc. Indiana Acad. Sci.*, 1922, 247—252).—Complete data are tabulated for the use of bromocresol-purple, bromothymol-blue, and phenol-red as indicators, whereby bacteria of the colon-typhoid group (*Bacillus coli, B. typhosus, B. dysenteriæ, B. paratyphosus A* and *B*, and *B. enteritidis*) can be distinguished in their formation of acid from dextrose, lactose, sucrose, maltose, raffinose, mannose, dulcitol, xylose, rhamnose, arabinose, lævulose, and galactose. The above indicators are mentioned in increasing order of sensitiveness. CHEMICAL ABSTRACTS.

Transformation of Carbon Compounds by *Bacillus pyocyaneus*. J. SUPNIEWSKI (*Compt. rend. Soc. Biol.*, 1923, 89, 1377—1379; from *Chem. Zentr.*, 1924, i, 1679).—Sodium acetate when added to cultures of *B. pyocyaneus* is rapidly decomposed, probably with formation of formaldehyde and formic acid. Acetaldehyde is oxidised to acetic acid. Acetone gives formic and acetic acids. Ethyl alcohol gives acetaldehyde and acetic acid. Lactic acid gives pyruvic and acetic acids, acetaldehyde, and carbonates. Glycerol is oxidised to carbon dioxide. Dextrose is rapidly attacked. Cultures containing aliphatic compounds with carboxyl groups become alkaline by oxidation of these groups, whilst compounds containing the groups —OH, =CO, or —CHO become acid through oxidation to acids. The limit on the alkaline side is p_H 8·8 and on the acid side p_H 6·6. G. W. R.

Transformation of Nitrogen Compounds by *Bacillus pyocyaneus*. J. SUPNIEWSKI (*Compt. rend. Soc. Biol.*, 1923, 89, 1379—1380; from *Chem. Zentr.*, 1924, i, 1679; cf. preceding abstract).—*B. pyocyaneus* readily assimilates ammoniacal and nitrate nitrogen, the oxygen in the latter case being also utilised. Carbamide is decomposed to ammonium carbonate by means of a urease. Glycine is not readily attacked. Asparagine is first deamidised with formation of ammonium aspartate and, ultimately, ammonium malate. Cyanogen compounds are assimilated after being converted into ammonium compounds. G. W. R.

Metabolism of Cyclic Compounds by *Bacillus pyocyaneus*. J. SUPNIEWSKI (*Biochem. Z.*, 1924, **146**, 522—535).—*B. pyocyaneus* is unable to utilise most benzene derivatives, nor are aminobenzenes suitable as sources of nitrogen. Salicin is decomposed, the dextrose residue being utilised and the saligenin oxidised to salicylic acid. Aliphatic and cyclic amino-acids are decomposed with destruction of the carboxyl group and liberation of ammonia. Tryptophan is decomposed with, apparently, the intermediate formation of anthranilic

acid. The bacillus acts very slowly on indole itself. Anthranilic acid is decomposed to form ammonium carbonate whilst *p*- and *m*-aminobenzoic acids are not attacked. These two last-mentioned acids together with *o*- and *m*-aminocinnamic acids do not serve as sources of carbon or nitrogen. J. P.

Oxidation and Reduction by *Pneumococcus*. I. Production of Peroxide by Anaërobic Cultures of *Pneumococcus* on Exposure to Air under Conditions not Permitting Active Growth. II. Production of Peroxide by Sterile Extracts of *Pneumococcus*. O. T. AVERY and J. M. NEILL (*J. Exp. Med.*, 1924, **39**, 347—355, 357—366).—I. When grown anaërobically, pneumococci form peroxide on exposure to molecular oxygen with a rapidity which varies with the condition of the culture; the effect is not dependent on active cell-growth.

II. At p_H 5—9, sterile extracts of unwashed cells form peroxide on exposure to the air. CHEMICAL ABSTRACTS.

Growth-inhibitory Substances in *Pneumococcus* Cultures. H. J. MORGAN and O. T. AVERY (*J. Exp. Med.*, 1924, **39**, 335—346).—A study of the effect of hydrogen peroxide on the growth of *Pneumococcus* and *Staphylococcus aureus*, and of the latter in filtrates from cultures of the former. CHEMICAL ABSTRACTS.

Chemical Evidence on the Phylogenetic Classification of the Tubercle Bacillus. E. R. LONG (*Amer. Rev. Tuberculosis*, 1923, **8**, 195—213).—The fairly definite animal tendencies of the tubercle bacillus are: a nucleic acid probably identical with that of the thymus, pancreas, sperm, and spleen. The basis, therefore, lies in the established presence of the pyrimidines, thymine, and cytosine, in tubercle bacillus nucleic acid, and the presence of a hexose, and the established absence of uracil. The fairly definite plant tendencies are: a marked chemosynthetic power in nitrogen metabolism; synthesising such complex substances as amino-acids and purine bases with no source of nitrogen other than ammonia. The less definite animal tendencies are: the said possession of lipins of the diamino-monophosphatide type, which so far have been described convincingly only in animals. The less definite plant tendencies are: the said content of hemicellulose or pentosans, made up of pentose units, which are typical plant substances, and an appreciable content of lauric acid, which has a wide plant distribution. CHEMICAL ABSTRACTS.

Enzymic Studies on Lactic Acid Bacilli. A. I. VIRTANEN (*Z. physiol. Chem.*, 1924, **134**, 300—319).—Lactic acid fermentation is a unimolecular reaction. Attempts to demonstrate a synthesis of hexose phosphate from mixtures of inorganic phosphate and dextrose or lactose were entirely negative, both with the living organisms and with dried preparations. Lævulose diphosphate was not affected by lactic acid bacilli. Catalase was entirely absent from the organisms. The living bacteria, but not the dried preparations, have the power of reducing methylene-blue; it is suggested

that the reducing power of milk towards methylene-blue is due partly to the presence of bacteria. C. R. H.

Production of Formaldehyde by Intestinal Bacteria. B. H. SHAW (*Brit. Med. J.*, 1924, I, 461—463).—From 0·0001 to 0·0015% of formaldehyde was produced by the action of various intestinal bacteria on peptone alone and admixed with lactose, dextrose, mannitol, or inulin. Bacteria do not appear to be capable of producing formaldehyde when oxygen is excluded. A. A. E.

Influence of Sodium Pyruvate on Phosphorescent Bacteria. A. BERTHELOT and G. AMOUREUX (*Bull. Soc. Chim. biol.*, 1924, 6, 336—337).—The luminosity of cultures of a species of phosphorescent bacterium (isolated from a marine fish) in a liquid medium was first depressed and afterwards much increased by the addition of sodium pyruvate at the rate of 4 g. per litre. Urea acted similarly, and a still greater effect was obtained with a mixture of urea and pyruvate. It is not yet known whether the pyruvate acts directly on the phenomenon of phosphorescence or whether it simply causes a greater development of the organism. C. T. G.

Culture of Spirochætes in Media containing Sodium Pyruvate. A. BERTHELOT and P. SÉGUIN (*Bull. Soc. Chim. biol.*, 1924, 6, 341).—Two species of spirochæte from the mouth—*Sp. dentium* and *Sp. tenuis*—which do not develop on ordinary serum-bouillon, grew and remained alive for more than a month in this medium with the addition of 2 to 10 drops of a 20% solution of sodium or potassium pyruvate to each tube. Such a medium is suitable for the maintenance of pure cultures of these organisms and is much more simple to prepare than Noguchi's medium. C. T. G.

Variations in Hydrogen-ion Concentration during the Assimilation of Ammoniacal Salts of Strong Acids by *Aspergillus repens*, de Bary. D. BACH (*Compt. rend.*, 1924, 178, 2194—2195).—The growth of this mould is inhibited by high hydrogen-ion concentration, and for this reason a medium containing ammonium chloride is deleterious, since it results in the liberation of hydrochloric acid. Any cause capable of retarding this increase of acidity increases value of the salt as a nutrient for the mould. A. COUSEN.

Preparation of Organic Acids by Biological Methods with the Help of Hyphenated Moulds. R. FALCK and VAN BEYMA THOE KINGMA (*Ber.*, 1924, 57, [*B*], 915—920).—A general account is given of the experimental technique necessary for the production of uniform results in the investigation of the production of acids from carbohydrates with the aid of moulds. An approximately 1% agar jelly is used as substrate into which the mould hyphæ do not penetrate more than a few millimetres. Dextrose is generally used as source of carbon, but may be replaced by other sugars, glycerol, starch, wood, or cellulose; the best concentration varies greatly with the particular type of mould. Ammonium nitrate

(0·16—0·32%) is the most suitable source of nitrogen; other nutrient salts are required in such small amount that their special provision is unnecessary if technical glucose is employed. For a given solution, the amount of acid formed in the unit of time is proportional within certain limits to the surface of the agar jelly. The production of acids by various types of *Aspergillus*, *Penicillium*, and *Citromyces* has been investigated. The black, brown, or pale brown types of *Aspergillus* yield acid freely, the yellow and greenish-yellow varieties moderately, whereas the pale or colourless types give little acid. The ultimate product is oxalic acid; the intermediate formation of citric acid is nearly always observed.

H. W.

Production of Gluconic Acid by Hyphenated Moulds. R. Falck and S. N. Kapur (*Ber.*, 1924, **57**, [*B*], 920—923; cf. preceding abstract).—Gluconic acid is produced by the action of four varieties of *Aspergillus niger*, *A. cinnamomens*, *A. fuscus*, and *Citromyces lactis* on solutions of glucose in the presence of calcium carbonate. The best conditions are secured by using relatively concentrated sugar and very dilute ammonium nitrate solutions, working at a low temperature, and interrupting the action when the calcium carbonate is dissolved, but previous to the separation of calcium citrate. The yield of acid is 50% of the sugar. The production of glycuronic acid could not be observed.

H. W.

Presence of Pyruvic acid in Cultures of certain *Mucors*. A. Berthelot and R. Pouisot (*Bull. Soc. Chim. biol.*, 1924, **6**, 343—344).—Pyruvic acid was detected in cultures of three species of *Mucor* in media containing sugars, after incubation for 15 days. In older cultures, pyruvic acid was not found. The production of this acid is no doubt one of the factors accounting for the favourable action of *Mucor* on the growth of yeast. C. T. G.

Formation of Pyruvic Acid and Ethyl Alcohol from Calcium Lactate by Yeasts. E. Kayser (*Bull. Soc. Chim. biol.*, 1924, **6**, 345—351).—Further details are given of work already published (cf. A., 1923, i, 986). The formation of the ethyl and amyl esters of acetic and valeric acids by various yeasts in media containing calcium lactate and mineral salts is confirmed. The alcohols were determined after saponification of the distillate from the cultures by a combination of the methods of Duclaux and Nicloux.

C. T. G.

Rôle of the Reaction of the Medium in Selective Fermentation. A. Fernbach and N. Schiller (*Compt. rend.*, 1924, **178**, 2196—2197).—The fermentation of sugar solutions by 8 types of yeast has been studied, and in each case it has been found that lævulose is at first attacked more readily than dextrose, until a point is reached, varying with the yeast employed and not occurring in the case of Sauternes yeast, at which the relative rate of attack is

reversed. It was found possible to modify the course of the fermentation in other cases than that of the Sauternes yeast by decreasing the acidity of the solution. A. COUSEN.

Enzymic Equilibria. I. H. VON EULER and K. JOSEPHSON (*Z. physiol. Chem.*, 1924, **136**, 30—44).—From a mathematical treatment of the results obtained in a study of the equilibria in aqueous systems of the type, methyl alcohol–dextrose–emulsin, and fatty acid–alcohol–lipase, it is concluded that a more satisfactory interpretation results from the assumption that an affinity exists between enzyme and reaction products as well as between enzyme and substrate. This applies even in the case of invertase showing a hydrolytic action only. J. P.

Co-zymase of Yeast. III. H. VON EULER and K. MYRBÄCK (*Z. physiol. Chem.*, 1924, **136**, 107—129).—The concentration, purification, and characterisation of co-zymase are described. A method has been devised for determining co-zymase, based on the measurement of the carbon dioxide evolved with zymase and dextrose under standard conditions at p_H=6·2—6·6. The fermentative power of dried yeast preparations is increased by the addition of co-zymase and also by the addition of washed inactive yeast free from the co-enzyme. The rate of fermentation therefore depends on the relative quantities of zymase and co-zymase, and it is assumed that the two together form a dissociable compound which constitutes the active enzyme. By the addition of either zymase or co-zymase the dissociation of this active compound is suppressed, resulting in an increase in the activity of the mixture. The results on the thermostability of co-zymase are similar to those arrived at by Tholin (A., 1922, i, 305). Co-zymase is decomposed rapidly in solutions more alkaline than p_H 10, shows maximum stability at p_H 7, and is still active in 0·5*N*-hydrochloric acid (p_H 0·6). Contrary to the view hitherto accepted, it was found that lead acetate is capable of precipitating the co-zymase to a greater or less extent according to the p_H of the solution. The co-zymase is not affected by hydrogen sulphide, but is inactivated by traces of lead. When lead acetate was added to yeast juice containing the co-zymase at p_H 6, the free phosphate and the hexosephosphate were precipitated and the co-zymase was found mainly in the filtrate. When the latter was brought to p_H 8·3—10·0 the co-zymase was almost completely precipitated. It could be recovered from the lead precipitate by suitable means and such fractional precipitation may be employed for purification. It can also be purified in a solution free from phosphate, by adsorption on alumina, which is almost quantitative at p_H 10, whilst in acid solutions no adsorption occurs. The alumina adsorbate is strongly active and the co-enzyme is not eluted therefrom by water or very dilute acids although it can be readily eluted quantitatively with 1% phosphate solution at p_H 6·3. D. R. N.

Nitrogen Content of Invertase. K. JOSEPHSON (*Z. physiol. Chem.*, 1924, **136**, 224—231).—In reply to Willstätter and Schneider

(this vol., i, 692), it is urged that proportionality between enzyme activity and nitrogen content is possible only when due regard is paid to the inactivation of part of the enzyme during the processes used for its purification. It is shown that, when the same yeast is used and experimental conditions are standardised, an approximate constancy exists for the ratio If/N. With simple assumptions, ratios for two of Willstätter's preparations show reasonable agreement.

O. O.

Affinity of Invertase for Different Sugars. III. Identity of Invertase and Raffinase. K. Josephson (*Z. physiol. Chem.*, 1924, **136**, 62—74; cf. Euler and Josephson, this vol., i, 467; Josephson, this vol., i, 801).—Invertase and raffinase show the same affinity constants to α- and β-dextrose, to lævulose, and to β-galactose, and these sugars inhibit the action of the two enzymes on sucrose and on raffinose to the same extent. It is concluded that invertase and raffinase are identical. Melibiose shows no affinity for invertase.

J. P.

Relative Specificity of Yeast Maltase. R. Willstätter, R. Kuhn, and H. Sobotka (*Z. physiol. Chem.*, 1924, **134**, 224—242).—The hydrolysis of α-methyl-, α-ethyl-, and α-phenyl-glucosides and of amygdalin by the maltase of yeasts from various sources was studied. The hydrolysis of α-ethylglucoside in some cases obeyed the law of a unimolecular reaction; in others the rate of reaction fell off more rapidly. In the case of α-phenylglucoside, the curve representing the course of the reaction corresponds with that already described for the hydrolysis of α-methylglucoside (A., 1921, i, 282). The power of different yeast-extracts to hydrolyse the α-glucosides is parallel with their rate of hydrolysis of amygdalin. All the specimens of maltase examined showed less affinity for the aliphatic glucosides than for α-phenylglucoside.

C. R. H.

Lipase of the Castor Oil Bean. R. Willstätter and E. Waldschmidt-Leitz (*Z. physiol. Chem.*, 1924, **134**, 161—223).—The enzyme was most active at a p_H of 4·7 to 5·0; its activity was unaffected by the addition of manganese salts and was inhibited by sodium chloride; the optimum temperature was 35°. An investigation of the kinetics of the reaction under constant physical conditions showed that its course was not regular.

The removal by means of organic solvents of the oil contained in the beans resulted in all cases in a serious loss of enzymic activity; moreover, the preparations so obtained were very unstable. This method of purification was therefore abandoned in favour of the separation, and drying in a vacuum desiccator or in an air current, of the "cream" obtained by centrifuging an aqueous emulsion of the pulverised beans. In this way there was far less loss, especially if the cream were mixed with a quantity of kieselguhr before drying. Further purification was effected by washing the "cream" with dilute alkali. The dried preparation finally obtained retained its activity for a fairly long period; it contained much protein but

no carbohydrate. The only marked difference in its elementary composition from that of the crude powdered beans was an increase in the phosphorus content.

The apparent increase in lipolytic activity during germination observed by previous authors (cf. A., 1903, i, 218; 1904, ii, 433) is due to a change in the character of the enzyme by which its optimum hydrogen-ion concentration is shifted to the alkaline side. (For distinction, the original enzyme is termed *spermatolipase*, and the altered one *blastolipase*.) The formation of blastolipase from the spermatolipase can also be brought about by the action of pepsin and by hydrolysis with acids. Dried preparations of blastolipase were much more stable than those of spermatolipase, and their synthetic action, on a mixture of glycerol and oleic acid, was considerably stronger. C. R. H.

Animal Carboxylase. A. Gottschalk (*Biochem. Z.*, 1924, **146**, 582—588).—Rabbit liver pulp to which pyruvic acid is added shows after incubation, both in the presence and in the absence of oxygen, more acetaldehyde formation than controls containing no added pyruvic acid. The presence of a carboxylase is inferred (cf. also Neuberg and Gottschalk, this vol., i, 785). J. P.

Methylated Proteins. I. Action of Proteolytic Enzymes on Methylated Proteins. T. Imai (*Z. physiol. Chem.*, 1924, **136**, 173—187).—When casein or edestin is methylated with methyl sulphate and sodium hydroxide at 20°, the methyl derivative, which is insoluble in alcohol and in ether, is obtained as an amorphous white powder easily soluble in water. These derivatives are hydrolysed by pepsin, trypsin, and erepsin, although to a much lesser extent compared with the unmethylated protein. D. R. N.

Methylated Proteins. II. Hydrolysis of Methylated Casein. T. Imai (*Z. physiol. Chem.*, 1924, **136**, 188—191).—A certain relation exists between the lysin content of a protein and the free amino groups in the protein molecule (cf. A., 1912, i, 1041; 1920, i, 687). If, therefore, methylated amino-acids could be isolated from the products of hydrolysis of a methylated protein, it could be readily ascertained which amino groups are free in the original molecule. Edlbacher (A., 1921, i, 199) obtained in the lysin fraction a considerable quantity of a syrupy mass from which he was not able to isolate any well-defined compound. This fraction has now been further examined. When a methylated protein is hydrolysed with proteolytic enzymes, from the products of hydrolysis histidine is obtained in traces, arginine in a small quantity, whilst a considerable amount is obtained as a syrupy mass in the lysin fraction, from which a crystalline platinum chloride double salt has been isolated. It is very easily soluble in water, and in methyl and ethyl alcohol. D. R. N.

Methylated Proteins. III. Action of Erepsin on Methylated Polypeptides. T. Imai (*Z. physiol. Chem.*, 1924, **136**, 192—204).—It is supposed that in methylated proteins the free amino groups are methylated whilst the imino groups are not

affected (A., 1920, i, 825). Owing to the relative difficulty of hydrolysis of methylated proteins by enzymes, it appeared probable that the ease of hydrolysis of the peptide linkings by proteolytic enzymes depended on their distance from the methylated amino groups. To establish this view the behaviour of the betaines of glycylglycine, diglycylglycine, and triglycylglycine towards erepsin has been studied. The first two are not attacked, whilst the latter is hydrolysed to a slight extent. D. R. N.

Action of Erepsin on Benzoylated Polypeptides. T. Imai (*Z. physiol. Chem.*, 1924, **136**, 205—213).—As the methylated polypeptides of glycine are only crystallisable with difficulty, the behaviour of the more easily crystallisable benzoylated polypeptides of glycine towards erepsin has been studied. Benzoylglycylglycine, in common with the methylated dipeptide, is not attacked whilst the benzoyl-di-, -tri-, and -tetra-glycylglycines are hydrolysed to different extents. It is uncertain which peptide linkings in these derivatives are attacked. D. R. N.

Comparison of certain Oxidising Enzymes of the Higher and Lower Plants. M. E. Robinson (*Biochem. J.*, 1924, **18**, 543—548).—The oxydases of the higher plants consist of three components, a pyrocatechol derivative and two enzymes—oxygenase and peroxydase. Those of the *Basidiomycetes* consists only of an enzyme-like peroxide and peroxydase. The experiments of Onslow on certain phanerogam oxydases and those of Gallagher on extractable plant phosphatides have been repeated and confirmed. Gallagher's interpretation of his results is criticised. S. S. Z.

Oxidising Enzymes. VII. Oxygenase of Higher Plants. M. W. Onslow (*Biochem. J.*, 1924, **18**, 549).—Polemical. It is reasserted that oxygenase catalyses the formation of peroxide; Gallagher's assertion that the blueing of guaiacum is due to the presence of an autoxidisable lecithin-like substance is criticised. S. S. Z.

Use of Guaiacol for Measuring the Activity of Oxydase Preparations. P. Fleury (*J. Pharm. Chim.*, 1924, [vii], **29**, 402—414).—Tetraguaiacoquinone, $[C_6H_3(OMe)O—]_4$, to which the red coloration given by the action of laccase on guaiacol is due, separates as a precipitate when the solution is kept and forms colloidal solutions, which readily coagulate, with water. It can be used for the purposes of colorimetric analysis, however, by extracting it with chloroform and comparing the colour of the solution with that of a 0·01*N*-solution of iodine. A solution of 46·5 mg. of guaiacoquinone in 1 litre of chloroform, obtained by extraction from aqueous solution, has the same colour as 0·01*N*-iodine solution, the thickness of the layer viewed in each case being 10 mm. The oxidation of guaiacol by air in the presence of laccase proceeds quantitatively, but the yield of guaiacoquinone varies between 72 and 95%, being influenced adversely by allowing the reaction to be prolonged, by the presence of an excess of guaiacol, by the alkalinity of the medium, and by raising the temperature. These

influences are negligible, however, under the conditions of the experiments described. The activity of the laccase remains practically unchanged at the end of the reaction. W. T. K. B.

Influence of *X*-Rays on Leucocytic Oxydases. P. Lemay, C. Guilbert, R. Petit, and L. Jaloustre (*Compt. rend.*, 1924, **178**, 1711—1713; cf. Maubert and others, A., 1923, i, 723; this vol., i, 808).—The activity of both direct and indirect leucocytic oxydases is increased by weak doses of *X*-rays, but whilst the direct oxydases remain stable and unchanged under the action of more powerful doses, the indirect oxydases are inactivated. The latter are not, however, destroyed, and they recover again a certain time after the cessation of radiation. M. S. B.

History of Carbon Dioxide Assimilation. F. Weigert (*Z. physikal. Chem.*, 1924, **109**, 79—80; cf. A., 1923, i, 1271).—A question of priority (cf. Warburg and Negelein, this vol., ii, 241). M. S. B.

Blackman's Reaction. O. Warburg and T. Uyesugi (*Biochem. Z.*, 1924, **146**, 486—492).—Using suspensions of the alga *Chlorella*, the influence of hydrogen cyanide and of various substituted urethanes on the Blackman reaction (rate of decomposition of carbon dioxide and liberation of oxygen in strong light), on the one hand, and on the decomposition of hydrogen peroxide and on respiration on the other, has been investigated. The parallelism between the two sets of results lends support to the views of Willstätter and Stoll ("Untersuchungen über die Assimilation der Kohlensäure," Berlin, 1918). J. P.

Influence of Acidity on Plant Growth without regard to other Factors. A. G. McCall (*J. Amer. Soc. Agron.*, 1923, **15**, 290—297).—A general review of recent work on soil reaction and the tolerance of acidity by plants in solution cultures and by bacteria in soils. Measurements of hydrogen-ion concentrations may prove more useful than lime requirement tests, but in practice the application of lime need not necessarily be carried to the point of neutralisation. E. M. C.

Effect of Hydroxyl-ion Concentration on the Growth of Walnut Roots. H. S. Reed and A. R. C. Haas (*Amer. J. Bot.*, 1924, **11**, 78—84).—Walnut seedlings are very sensitive to the absence of calcium from the culture solution. The injury to walnut roots from solutions of high p_H values is due principally to calcium starvation rather than to the effect of high concentration of hydroxyl ions on the plant. A. A. E.

Effect of Salts on the Intake of Inorganic Elements and on the Buffer System of the Plant. D. R. Hoagland and J. C. Martin (*California Agr. Expt. Sta., Tech. Paper*, 1923, 8, 26 pp.).—Sodium chloride and sodium sulphate, added to a culture solution, caused marked alteration in the composition of the barley plant, tending to decrease the absorption of calcium, magnesium, and potassium. Sodium and chlorine may be absorbed and stored by the barley

plant in relatively large quantities. The sulphate ion is taken up by several plants less rapidly than the chloride ion. No definite alkali tolerance for different plants can be established because of the important modifying effects of environmental factors. The buffer effects of the expressed sap of stems and leaves was greater than that of roots. Rapid and extreme changes in reaction of the expressed root sap were caused by the addition of sodium hydrogen carbonate to the culture solutions. Calcium chloride produced appreciable changes in the reaction and buffer effects of plant juices. Sodium nitrate increased the alkalinity of the expressed root sap, with a slight accompanying injury resembling that induced by sodium hydrogen carbonate. E. M. C.

Effect of Sodium Chloride and Calcium Chloride upon Growth and Composition of Young Orange Trees. H. S. Reed and A. R. C. Haas (*California Agr. Expt. Sta., Tech. Paper*, 1923, 4, 21 pp.).—Orange trees were grown in various nutrient solutions in sand and the distribution throughout the plant of nitrogen, calcium, sodium, and potassium was determined. Physiological disturbances developed in a few months in the trees grown in incomplete nutrient solutions. Omission of calcium caused spotting and shedding of the leaves and the repeated development of new buds. In such trees, the calcium was retained principally in the trunks and roots, and was present only in small amounts in the leaves, shoots, and rootlets, indicating a low mobility of calcium. In plants grown in full nutrient solutions, the percentage of calcium in the ash was fairly constant throughout the plant. The percentage of potash was high in all parts of the trees. In the presence of calcium chloride vigorous growth was made even when considerable amounts of sodium chloride were also present. E. M. C.

Nutrition of the Potato Plant with Special Reference to Water Cultures. W. Newton (*J. Amer. Soc. Agron.*, 1923, **15**, 392—399).—Potato plants were rapidly injured by the omission of calcium salts from the solution, but showed an increased yield of tubers when potassium was omitted. It is suggested that the value of potash fertilisers may be due in part to the indirect effect of increasing the calcium content of the soil solution. E. M. C.

Plant Colloids. XV. Amylopectins Prepared from Different Starches. M. Samec, M. Minaeff, and N. Ronžin (*Koll. Chem. Beihefte*, 1924, **19**, 203—212).—Amylopectins of various origin differ in the appearance, conductivity, viscosity, and hydrogen-ion concentration of the aqueous solutions, and in the phosphorus content, titratable acidity, and amount of alkali combined with one g.-atom of phosphorus. The amylopectins from underground storage organs (potato, arrowroot, and tapioca) and from seeds (maize, rice, wheat) form two distinct groups. These differences do not depend on variations in the cations associated with the amylophosphoric acids, since they are maintained in starches washed with dilute hydrochloric acid. Synthetic amylopectins prepared from the different starches are closely analogous.

E. M. C.

Occurrence of Alkaloids in Nature. I. Common Occurrence of Alkaloids and Tannides. L. ROSENTHALER and M. MOSEMANN (*Schweiz. Apoth.-Ztg.*, 1924, **62**, 13—15, 29—31, 48—50; from *Chem. Zentr.*, 1924, i, 1678).—In a considerable number of cases alkaloids and tannides occur together in the same cells. It is not, however, always necessary to assume the existence of alkaloid–tannide compounds. Such compounds may be present where the presence of alkaloids is not shown by the usual tests. Many alkaloids and tannides are products of excretion and insoluble alkaloid–tannide compounds may also be regarded as such. They may, however, have some physiological function. G. W. R.

Phytosterols of the Endosperm of Corn [Maize]. R. J. ANDERSON (*J. Amer. Chem. Soc.*, 1924, **46**, 1450—1460).—Maize gluten (23 kg.) was extracted with ether-alcohol (1 : 1), and the extract, which contained some free phytosterol, yielded, on hydrolysis with alcoholic potassium hydroxide, crude, crystalline phytosterol (55 g.) and an oil (30 g.). *Dihydrositosterol*, $C_{27}H_{47}OH,H_2O$, m. p. 139° (anhydrous, m. p. 141°), $[\alpha]_D^{20}$ +24·23° in chloroform, was obtained from the crude phytosterol by 39 crystallisations from alcohol, and hydrolysis of the purified *acetyl* derivative, which formed large hexagonal plates, m. p. 138°, $[\alpha]_D^{20}$ +14·41°. The accompanying sitosterol could not be completely removed by crystallisation, but was extracted from the chloroform solution of the acetyl derivatives by concentrated sulphuric acid, dihydrositosterol then being obtained of $[\alpha]_D^{20}$ +25·04°. The crude phytosterol (15·6 g.) obtained similarly from maize bran (15 kg.) is relatively rich in dihydrositosterol. Dihydrositosterol does not give the Liebermann-Burchard reaction, and does not absorb bromine. F. G. W.

Aleurone Cells of Cereals. E. B. BENNION (*Cereal Chem.*, 1924, **1**, 138—148).—The author has separated the aleurone layer from barley and wheat, and made elementary analyses on products obtained by extraction with sodium chloride solution and alcohol. The aleurone cells of barley contain only small quantities of fatty matter, but those of wheat contain an oil and a white, waxy material, probably phytosterol. The residue after extraction with alcohol was rich in nitrogen and ash. E. M. C.

The Genus *Mentha*. *Mentha piperita*. F. J. BACON, G. C. JENISON, and R. E. KREMERS (*J. Amer. Pharm. Assoc.*, 1923, **12**, 1075—1077).—Methyl*cyclo*hexanone is not constantly present and it is possible that its reported occurrence is due to the treatment to which the oil was subjected. Its precursor, pulegone (and possibly piperitone) is constantly present. It is suggested that menthenone is first formed and that menthol and menthone are formed from it by reduction. Aldehydes are present in only small proportions in the natural oil and are mostly eliminated in the refining processes. From 5454·5 kg. of oil, 500 g. of *iso*valeraldehyde were obtained. CHEMICAL ABSTRACTS.

Constituents of Ragweed Pollen. F. W. HEYL (*J. Amer. Pharm. Assoc.*, 1923, **12**, 669—676; cf. A., 1922, i, 1224).—The

ethereal extract of ragweed pollen contained formic, acetic, valeric, lauric, oleic, linoleic, palmitic, and myristic acids, and an unsaturated acid, $C_{10}H_{18}O_2$; the alcoholic extract contained a mixture of phosphatides. The acetone-insoluble lipin was obtained by recrystallisation. The water-soluble portion of the alcoholic extract contained adenine, betaine, sucrose, lævulose, and a trace of guanosine. With the exception of the colouring matters and possibly a proteose, none of the 27 substances isolated appears to be a chemical specialisation of the pollen cell. CHEMICAL ABSTRACTS.

Accumulation of Iron and Aluminium Compounds in Maize Plants and its Probable Relation to Root Rots. II. G. N. HOFFER and J. F. TROST (*J. Amer. Soc. Agron.*, 1923, **15**, 323—331).—The accumulation of iron and aluminium compounds in the nodal tissues of maize plants is affected by soil conditions. The accumulation of aluminium and to a less extent of iron in the plants is associated with retarded growth and increased susceptibility of certain strains to root rots. E. M. C.

Action of Metabolic End-products on Plants. III. Action of Nitrogen-free End-products of Plant Metabolism (Ethereal Oils, Terpenes, etc.) on the Germination of Seeds. W. SIGMUND (*Biochem. Z.*, 1924, **146**, 389—419).—An investigation of the influence of various ethereal oils and terpenes on the germination of vetch, wheat, and rape seeds. Mustard oil proved most toxic, followed by clove and caraway oil; the oils of aniseed, fennel, geranium, peppermint, rosemary, and thyme, although less active than the first three, also definitely inhibited germination. Oil of garlic was toxic in the form of vapour but much less so in solution, whilst oil of turpentine gave similar results. The oils of bergamot, cedar, citron, eucalyptus, rue, and juniper berry were practically devoid of effect in solution. The results obtained with individual constituents of the oils were as follows: Hydrocarbons:—cymene, *d*- and *l*-limonene, *d*- and *l*-pinene, and styrene, no action. Alcohols:—borneol, linaloöl, menthol, terpin hydrate, no action; terpineol, toxic. Aldehydes:—benzaldehyde, citral, cinnamaldehyde, very toxic; anisaldehyde, somewhat less toxic; *iso*valeraldehyde and vanillin least toxic. Ketones:—in order of diminishing toxicity, carvone, camphor, fenchone, cineole. Phenols:—carvacrol, thymol, apiole, safrole, very toxic; anethole, weakly toxic. Acid:—anisic acid, little or no action. Ester:—methyl salicylate, toxic. J. P.

Action of Formates on the Growth of certain Plants in Pot Cultures. C. RICHET, junr. (*Compt. rend.*, 1924, **178**, 1922—1923).—The addition of small amounts of sodium or calcium formate to soil, either at the time of sowing or at the commencement of germination, increased the germinating power of wheat and barley by 10—20%. There was no significant increase in the weight of the shoots. E. M. C.

Influence of Temperature of the Soil on the Relation of Roots to Oxygen. CANNON (*Science*, 1923, **58**, 331).—The maximum, optimum, and minimum temperatures for the growth

of roots in normally aërated soil are altered under conditions of diminished oxygen supply. The rate of root growth with a given oxygen supply as compared with the rate under normal aëration decreases with increase of temperature of the soil.

Typical results are given with regard to several species of plants, and it is suggested that investigations on the oxygen relation of roots would give results of considerable value from an ecological point of view. C. T. G.

Action of Salt Solutions on the Soil. II. O. NOLTE and E. SANDER (*Landw. Versuchs-Stat.*, 1924, **102**, 219—225).—On theoretical grounds and as the result of earlier work (cf. A., 1921, i, 914), it was expected that the rate of percolation of a salt solution through a column of soil, *i.e.*, the permeability of the soil, would bear a definite relation to the reaction of the solution. Tables and graphs are presented showing the changes in the p_H values (determined electrometrically), week by week, of the percolate from a column of soil, treated for 4 weeks with water, followed by a 1% salt solution for 4 weeks and then by water again for a final period. Uni-, bi-, and ter-valent salts (chlorides) are included. A close connexion between the hydrogen-ion concentration and the permeability is indicated. Similar changes in reaction were recorded on percolating powdered quartz with potassium chloride solution. C. T. G.

Formation of Sodium Carbonate in Soils. A. B. CUMMINS and W. P. KELLEY (*California Agr. Expt. Sta., Tech. Paper*, 1923, 3, 35 pp.).—An explanation is suggested for the observation that semi-arid soils, on treatment with sodium chloride solutions and subsequent leaching, swell and become impervious, yielding a dark, alkaline percolate. The sodium silicate complexes (" absorbates ") formed by the displacement of calcium and other bases by sodium are less stable, more soluble, and more readily hydrolysed than the corresponding calcium complexes. The alkalinity results from the hydrolysis of these " absorbates " on the reduction of the salt concentration by leaching and an interaction with the carbon dioxide of the soil solution. Some of the products of hydrolysis tend to assume the colloidal state. The presence of calcium carbonate is not essential for the formation of sodium carbonate in soils. Certain soils from humid regions react similarly to, but not so markedly as, the semi-arid soils. Alkalinity was also developed by granite and pure mineral silicates after similar treatment. Sodium chloride solutions more concentrated than 0·01*N* were able to form hydrolysable compounds in soil, and the concentration of sodium chloride needed to be reduced to about one-half by leaching before alkalinity developed. Calcium salts in sufficient concentration prevented the formation of hydrolysable sodium " absorbates," and tended to prevent the hydrolysis of such compounds when already formed. E. M. C.

Removal of Sodium Carbonate from Soils. W. P. KELLEY and E. E. THOMAS (*California Agr. Expt. Sta., Tech. Paper*, 1923, 1, 23 pp.).—Active oxidation of added sulphur took place in

alkali soils containing relatively high concentrations of sodium salts and ultimately removed the soluble carbonates in all but one of the soils studied. Calcium sulphate reduced the soluble carbonates, but failed to remove the alkalinity except when it was used in conjunction with leaching. Sulphuric acid was somewhat more effective than the sulphur oxidation products and considerably more so than calcium sulphate. The amounts of these materials needed is considerably greater than the soluble carbonate content, indicating that they interact with silicates and other alkaline compounds. In view of the importance of the subsoil, treatment with calcium sulphate followed by leaching seems to be the most successful for black alkali soils. Preliminary experiments indicated that ferrous sulphate and alum might also prove useful. E. M. C.

Alkali Soil Investigations. I. Colloidal Phenomena. J. S. JOFFE and H. C. MCLEAN (*Soil Sci.*, 1924, **17**, 395—409).—The oxidation of sulphur added to an alkali soil resulted in an increased surface tension of the aqueous extracts, and increased rates of capillary rise of water and percolation of water through the soil. E. M. C.

Importance of Hydrogen-ion Concentration Control in Physico-chemical Studies of Heavy Soils. R. BRADFIELD (*Soil Sci.*, 1924, **17**, 411—422).—The amount of electrolyte required to flocculate a colloidal clay solution can only be defined with reference to a definite p_H value. The initial reaction of the clay is an important factor in determining its behaviour at other p_H values; with alkaline flocculants, a part is utilised in neutralising an acid clay and the concentration of the clay thus becomes important. Different acids flocculate colloidal clay solutions at about the same concentration of hydrogen ions, but the amounts of acid needed may vary widely if expressed in terms of the titratable acidity. The hydrogen-ion concentration at equilibrium plays an important part in determining the absorption and exchange of bases between clay and salts. A colloidal clay was treated with various mixtures of potassium chloride and hydroxide, such that the potassium was 0·1*N*. The amount of potassium absorbed increased steadily with the p_H value. The amounts of alumina, silica, and ferric oxide liberated decreased with decreasing hydrogen-ion concentration, and became negligible near the neutral point. With increasing alkalinity, silica and alumina were again made soluble. The amounts of calcium and magnesium oxides liberated fell off with decreasing acidity and remained negligible in the more alkaline solutions. The difference between the absorption and liberation of bases, expressed in equivalent amounts, closely followed the equilibrium p_H value over a wide range and became zero for the value corresponding with that of the original clay solution.

E. M. C.

Active Acidity of Soils. E. T. WHERRY (*J. Wash. Acad. Sci.*, 1924, **14**, 207—211).—A restatement of the importance of the measurement of the hydrogen-ion concentration or "active acidity" of soil suspensions. E. M. C.

Methods of Diagnosing [Soil] Toxicity. P. L. GILE (*J. Amer. Soc. Agron.*, 1923, **15**, 305—312).—The author reviews the experiments on the relationship of aluminium salts to soil acidity. It is suggested that no specific toxicity of aluminium ions has been established and that the importance of the soil reaction is connected with its effect on the availability of different nutrients.

E. M. C.

Inorganic Substances, especially Aluminium, in Relation to the Activities of Soil Micro-organisms. WHITING (*J. Amer. Soc. Agron.*, 1923, **15**, 277).—A discussion of recent American work on the part played by aluminium in the occurrence of acidity and toxicity in soils and its influence on the biological activity of soil organisms. A summary of "concordant results" and of "results in need of verification and further investigation" is included.

C. T. G.

Effect of certain Potassium Fertilisers on Ammonification, Nitrification, and Crop Production. VAUDECAVEYE (*J. Amer. Soc. Agron.*, 1923, **15**, 415).—An account of pot-culture experiments on the effects of organic manure, lime, kainit, and potassium chloride and sulphate on ammonification, nitrification, and crop yield. Potassium fertilisers caused large increases in nitrification, but had little effect on ammonification. A definite relationship is shown to exist between bacterial activities and the production of soluble potassium in the soil.

C. T. G.

Microbiological Analysis of Soil as an Index of Soil Fertility. VIII. Decomposition of Cellulose. S. A. WAKSMAN and O. HEUKELEKIAN (*Soil Sci.*, 1924, **17**, 275—291).—There is a definite relation between the amount of cellulose decomposed in the soil by micro-organisms and the nitrogen assimilated, the available nitrogen becoming the controlling factor. Differences in the amount of cellulose decomposed in soils of different fertility are due to differences in the availability of the nitrogen and not to variations in the micro-flora, since all soils contain organisms able to attack cellulose. In acid soils the fungi are chiefly concerned, whilst in limed and neutral soils bacteria and probably actinomycetes also play an active part.

The cellulose-decomposing power of a soil determined with and without addition of sodium nitrate and with and without addition of calcium carbonate and mineral salts can be used to assist in the differentiation of soil fertility. The breaking down of cellulose (finely-divided filter-paper) may be followed by measuring the carbon dioxide evolved during a given time; or, the residual cellulose in the soil after incubation may be determined by the use of Schweitzer's reagent according to the method of Charpentier (*Diss.*, Helsingfors, 1921). Detailed procedures are suggested.

C. T. G.